

## BIROn - Birkbeck Institutional Research Online

Holtvoeth, J. and Whiteside, J.H. and Engels, Stefan and Freitas, F.S. and Grice, K. and Greenwood, P. and Johnson, S. and Kendall, I. and Lengger, S.K. and Lücke, A. and Mayr, C. and Naafs, B.D.A. and Rohrssen, M. and Sepúlveda, J. (2019) The paleolimnologist's guide to compound-specific stable isotope analysis - An introduction to principles and applications of CSIA for quaternary lake sediments. *Quaternary Science Reviews* 207 , pp. 101-133. ISSN 0277-3791.

Downloaded from: <https://eprints.bbk.ac.uk/id/eprint/26153/>

*Usage Guidelines:*

Please refer to usage guidelines at <https://eprints.bbk.ac.uk/policies.html>  
contact [lib-eprints@bbk.ac.uk](mailto:lib-eprints@bbk.ac.uk).

or alternatively

**The paleolimnologist's guide to compound-specific stable isotope analysis – an introduction to principles and applications of CSIA for Quaternary lake sediments**

Jens Holtvoeth<sup>1,2\*‡</sup>, Jessica H. Whiteside<sup>3\*‡</sup>, Stefan Engels<sup>4,5</sup>, Felipe Sales de Freitas<sup>1,2</sup>, Kliti Grice<sup>6</sup>, Paul Greenwood<sup>6,7</sup>, Sean Johnson<sup>8</sup>, Iain Kendall<sup>1</sup>, Sabine K. Lengger<sup>1,9</sup>, Andreas Lücke<sup>10</sup>, Christoph Mayr<sup>11</sup>, B. David A. Naafs<sup>1</sup>, Megan Rohrsen<sup>12</sup>, Julio Sepúlveda<sup>13</sup>

<sup>1</sup> Organic Geochemistry Unit, School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

<sup>2</sup> School of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, UK

<sup>3</sup> Ocean and Earth Science, National Oceanography Centre Southampton, University of Southampton, Waterfront Campus, SO14 3ZH, UK

<sup>4</sup> School of Geography, University of Nottingham, Nottingham, NG7 2RD, UK

<sup>5</sup> Department of Geography, Birkbeck, University of London, London, WC1H 9EZ, UK

<sup>6</sup> Department of Chemistry, Curtin University, Western Australia Organic and Isotope Geochemistry Centre, The Institute for Geoscience Research, School of Earth and Planetary Science, Perth, WA 6845, Australia

<sup>7</sup> Centre for Exploration Targeting and West Australian Biogeochemistry Centre, University of Western Australia, Crawley 6009, Australia

<sup>8</sup> Irish Centre for Research in Applied Geosciences, University College Dublin, Dublin, 4, Ireland

<sup>9</sup> School of Geography, Earth and Environmental Sciences, Plymouth University, Plymouth, PL4 8AA, UK

<sup>10</sup> Institute of Bio- and Geosciences, Agrosphere Institute (IBG-3), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

<sup>11</sup> Institute of Geography, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

<sup>12</sup> Department of Earth and Atmospheric Sciences, Central Michigan University, Mount Pleasant, MI 48859, USA

<sup>13</sup> Organic Geochemistry Laboratory, Geological Sciences and Institute for Arctic and Alpine Research, University of Colorado Boulder, CO 80309-0450, USA

\*corresponding authors

‡These authors contributed equally to the manuscript.

**ABSTRACT**

The stable isotope composition of key chemical elements for life on Earth (e.g., carbon, hydrogen, nitrogen, oxygen, sulfur) tracks changes in fluxes and turnover of these elements

in the biogeosphere. Over the past 15 to 20 years, the potential to measure these isotopic compositions for individual, source-specific organic molecules (biomarkers) and to link them to a range of environmental conditions and processes has been unlocked and amplified by increasingly sensitive, affordable and wide-spread analytical technology. Paleoenvironmental research has seen enormous step-changes in our understanding of past ecosystem dynamics. Vital to these paradigm shifts is the need for well-constrained modern and recent analogues. Through increased understanding of these environments and their biological pathways we can successfully unravel past climatic changes and associated ecosystem adaption.

With this review, we aim to introduce scientists working in the field of Quaternary paleolimnology to the tools that compound-specific isotope analysis (CSIA) provides for the gain of information on biogeochemical conditions in ancient environments. We provide information on fundamental principles and applications of novel and established CSIA applications based on the carbon, hydrogen, nitrogen, oxygen and sulfur isotopic composition of biomarkers. While biosynthesis, sources and associated isotope fractionation patterns of compounds such as *n*-alkanes are relatively well-constrained, new applications emerge from the increasing use of functionalized alkyl lipids, steroids, hopanoids, isoprenoids, GDGTs, pigments or cellulose. Biosynthesis and fractionation are not always fully understood. However, although analytical challenges remain, the future potential of deeper insights into ecosystem dynamics from the study of these compounds is also emerging.

**KEYWORDS:** stable isotopes, global, paleoclimatology

## 1 INTRODUCTION

The key elements that form organic matter on Earth, carbon, hydrogen, oxygen and nitrogen, occur in the form of two (C, H, N) or three (O) stable isotopes as determined by the number of neutrons in their nuclei, with the lighter isotope dominating. Each chemical reaction during the formation of organic matter and each phase transition (e.g., evaporation) changes the isotope distribution of the product (organic molecule, water vapour) by discriminating against the heavier (C, H, O) or, in some cases, lighter (N) isotopes. Thus, as these elements, and others such as sulfur, pass through biogeochemical cycles, their isotopic composition in a specific molecular and environmental context carries information on where they originally came from and how they got there. The determination of stable isotope ratios in an organic molecule therefore provides a tool to investigate and understand modern-day elemental cycling, thereby aiding our ability to reconstruct the variability of past element fluxes and the associated environmental drivers (for an introduction to stable isotope geochemistry see, e.g., Galimov,

1985; Hoefs, 2004). On a global scale, isotope distributions of carbon, oxygen and hydrogen vary over time, depending on the amounts of carbon dioxide and water stored in the major reservoirs, ocean water, atmosphere and polar ice caps or, on geological time scales, in rocks. Over the past five decades, stable carbon and oxygen isotope data from marine carbonates and ice cores, for example, has been fundamental in improving our understanding of the biogeosphere's response to external and internal forcing and associated changes in elemental fluxes such as the transfer of carbon from the atmosphere to the ocean. More recently, isotope analysis of individual biological compounds, i.e. compound-specific isotope analysis (CSIA) has allowed geoscientists to zoom in on processes involving organic matter transformation on much smaller scales and to study element cycling within individual ecosystems, from primary producer to ultimate microbial degrader and mineralisation. The improved understanding of how certain ecosystem changes can modify the isotopic fingerprint of organic molecules in sedimentary archives has resulted in the development of CSI-based proxies that document the adaption of the biosphere to the variability of key environmental parameters such as temperature or moisture supply. Some CSI proxies in fact respond to changes in these parameters directly, such as the hydrogen and oxygen isotope composition of meteoric water that is reflected in the isotope composition of biomarkers synthesized through the uptake of water and a carbon substrate (e.g., leaf-wax lipids, cellulose; Sauer et al., 2001a; Wolfe et al., 2001, 2007; Sachse et al., 2012). Many of the concepts, methodologies and paleoenvironmental proxies have originally been developed and applied in marine research, due to the fact that the global ocean is the most extensive ecosystem on Earth, with relatively well understood ecological boundary conditions, as compared to lakes, which feature specific ecological conditions that rarely match from one lake to another. However, since analytical facilities have become more widely available and the calibration of CSI data for applications in diverse lacustrine systems more affordable, an increasing number of lacustrine paleoenvironmental research projects now include CSIA, supporting established palynological or bulk geochemical data and thereby also bridging the (still existing) gaps between the various scientific communities.

This review aims to introduce CSIA as a prospective and increasingly popular tool to scientists in the field of paleolimnology who are practitioners of paleolimnology rather than specialized biogeochemists, involved in interdisciplinary studies and aiming for an improved understanding of the basic principles that control the proxy data they are dealing with or might want to produce themselves. The rapid expansion of diverse applications of CSIA has produced a plethora of research outputs, including recent reviews (i.e., Castañeda and Schouten, 2011; Sessions, 2016; Diefendorf and Freimuth, 2017) that provide detailed information on either individual isotopes or specific compound classes in both marine and

terrestrial settings. Here we provide an encompassing overview of CSIA (C,N,H,S) from an extensive spectrum of compounds for reconstructing Quaternary environmental change specifically from limnic settings, guiding the reader towards a more focused literature base with key case studies (summarized in Table 1). We include an introduction into the biosynthesis of the relevant biomarkers since isotope fractionation during biosynthesis is a key factor with regard to the ultimate stable isotope distribution in an organic molecule, in addition to the environmental factors driving the isotopic composition of the substrates used by primary producers. The desire for an improved understanding of proxy variability and sensitivity links paleoenvironmental sciences to studies of biogeochemical processes in modern ecosystems and food webs. Some of the CSI applications introduced here, for example, those using amino acids, pigment or sulfur-containing compounds, still are at the stage of development where further study of modern biogeochemical processes alongside pioneering paleoenvironmental research and methodological advances will help to develop their full potential, which also means that there are merits still to be gained. We thus hope our approach will help investigators new to the field to understand the relevance and power of isotope-based proxies and potentially inspires new ventures into one of the most dynamic realms of paleoenvironmental sciences.

In the following, we first provide an overview of the fundamental principles of isotope fractionation in biogeochemical cycles, followed by sections that introduce and discuss specific compound classes for which environmental proxies are well established (e.g., alkyl lipids) and less well-known compound classes or individual compounds (e.g., cellulose), with information on their various sources and CSIA applications. Although bulk elemental isotope analyses ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) provide useful paleoenvironmental information, particularly in combination with compound-specific isotopes, we will not review this area as it is well covered by other recent contributions (e.g., Sessions, 2016; Diefendorf and Freimuth, 2017).

## **2 STABLE ISOTOPE DISTRIBUTION, FRACTIONATION AND ANALYSIS**

### **2.1 Isotopes in the biogeosphere**

Photosynthetic and chemoautotrophic primary producers form the ultimate base of aquatic and terrestrial food chains, transforming molecular or elemental inorganic substrates (e.g.,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2$ ) and water into biomass. Biochemically speaking, life on Earth is essentially composed of carbon, hydrogen, oxygen, nitrogen and phosphorous, with a bulk stoichiometry, e.g., of the most important autotrophic producers of biomass, marine algae, of  $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$  (Redfield, 1958). Each autotrophic organism taps into specific reservoirs of the elements required in which the heavier stable isotopes, i.e.  $^{13}\text{C}$ ,  $^2\text{H}$ ,  $^{18}\text{O}$ ,  $^{15}\text{N}$ , are present in specific proportions. These proportions vary for each reservoir, depending on physical conditions and variable exchange with other reservoirs (e.g., proportions of  $\text{CO}_2$  with heavy

carbon and/or oxygen atoms in the atmosphere or the ocean vary across glacial-interglacial cycles, depending on temperature and evaporation rates; e.g., Hayes et al., 1999). Once a substrate has been taken up by an organism it will be fully or partially incorporated into organic molecules by enzymes. Enzymatic activity discriminates against the heavier (C, H, O) or, in case of nitrogen, lighter isotopes of reactants, leading to a different relative abundance of the light and heavy isotopes of the product, i.e. the isotope fractionation factor  $\epsilon$  (Hayes et al., 1989; Popp et al., 1989), discussed in more detail below. Hydrogen and nitrogen are also frequently exchanged between the compound that is biosynthesized and the operating enzyme. For example, during the biosynthesis of major lipid compound classes in a photosynthetic organism, enzymatic reactions involving nicotinamide adenine dinucleotide phosphate (NADPH) lead to repeated addition of isotopically light hydrogen (i.e.  $^1\text{H}$  rather than  $^2\text{H}$ ) to the synthesized lipid (e.g., Smith and Epstein 1970; Luo et al., 1991; see also Fig. 1).

Thus, the isotope composition of an element in biomass from primary production reflects the specific isotope composition of the reservoir and substrate and, through the fractionation factor between original substrate and synthesized biomass, the level and pathway of metabolic processing. Heterotrophic organisms consuming biomass of a certain isotope composition will again increase the fractionation factor to a certain extent when incorporating organic compounds into their own body tissue, either directly (little fractionation) or through further metabolic processing (additional fractionation; see, e.g., DeNiro and Epstein, 1978; Peterson and Fry, 1987).

Reactions between reduced inorganic sulfur and organic compounds in sediments are considered to be important for organic matter preservation. The fractionation of sulfur is a useful tracer of sulfurization reactions post-deposition, which often occur in the presence of strong pore water isotopic gradients, typically driven by microbial sulfate reduction, active during deposition and sedimentation (Habicht and Canfield, 1997; Kraal et al., 2013). Prior studies have looked at bulk sedimentary OM to understand fractionation as a function of sulfidization reactions between authigenic sulfide, and residual organosulfur compounds (Amrani and Aizenshtat, 2004; Riedinger et al., 2017; Pärn et al., 2018). However, enhanced ability to measure compound-specific sulfur isotopic compositions of volatile organosulfur compounds, co-eval pore water, sulfides forming, and the residual organic matter has greatly enabled our ability to understand the processes that govern sulfur cycling and diagenetic processes in both modern and ancient sediments.

## **2.2 Compound-specific isotope analysis (CSIA)**

Compound-specific isotope analysis (CSIA) provides the opportunity to trace the basic elements (C, H, N, S) through primary biosynthetic processes, food web dynamics and

heterotrophic microbial degradation to burial in the sedimentary archive (Matthews and Hayes, 1978). Quantifying these elemental fluxes underpins reconstructions of environmental dynamics and is key to the field of paleoenvironmental science. In recent years, applications of CSIA proxies to paleoenvironmental studies have gained increasing traction as our understanding of the biological and physical/chemical controls of isotopic fractionation improves (e.g., through studies of isotope fractionation in modern systems and mesocosm experiments). At the same time, analytical facilities are becoming more sensitive, automated and economical and therefore more widely available.

CSIA has now been successfully used to reconstruct changes in organic matter sources as well as to record the response of organisms to changes in temperature and moisture supply, air mass handling, shifts in food webs and diets, phytoplankton community shifts, water chemistry, redox chemistry, carbon cycling, methane cycling, vegetation change, and paleohydrology (see Table 1 for references).

Many CSIA methods start with common lipid extraction techniques such as microwave-assisted extraction (MAE), accelerated solvent extraction (ASE), ultrasonication, or Soxhlet extraction, using a range of organic solvent combinations and in some cases an added aqueous buffer. The protocols mainly differ in the processing of the total lipid extract (TLE) in order to purify the various target compounds, which typically includes separation of polar and non-polar compounds or of aliphatic hydrocarbons, aromatic hydrocarbons and alcohols (e.g., Sauer et al., 2001b). Individual compounds are commonly identified by gas chromatography–mass spectrometry (GC-MS) through their specific mass spectra and analysed by gas chromatography-isotope ratio mass spectrometry, with either a combustion or thermal conversion interface (GC-C-IRMS, GC-TC-IRMS; Hayes et al., 1989; Freeman et al., 1990; Hilkert et al., 1999), and by high-performance liquid chromatography-isotope ratio mass spectrometry (LC-IRMS; Boschker et al., 2008) to determine their isotopic composition. The latter is expressed as the divergence of the ratio of the heavier isotope over the lighter isotope from the equivalent ratio in a standardised reference material ( $\delta$ -annotation) as shown for carbon below (Eq. 1):

$$\delta^{13}\text{C} = \left( \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right) * 1000 \quad \textbf{Equation 1}$$

The international reference standards are Vienna Peedee Belemnite (VPDB) for  $^{13}\text{C}$ , Vienna Standard Mean Ocean Water (SMOW) for  $^2\text{H}$ , atmospheric  $\text{N}_2$  (AIR) for  $^{15}\text{N}$  and Vienna Canyon Diablo Troilite (V-CDT) for  $^{34}\text{S}$ . A comprehensive compilation of CSIA methodologies, including details on instrumentation, has been published by Jochmann and Schmidt (2011).

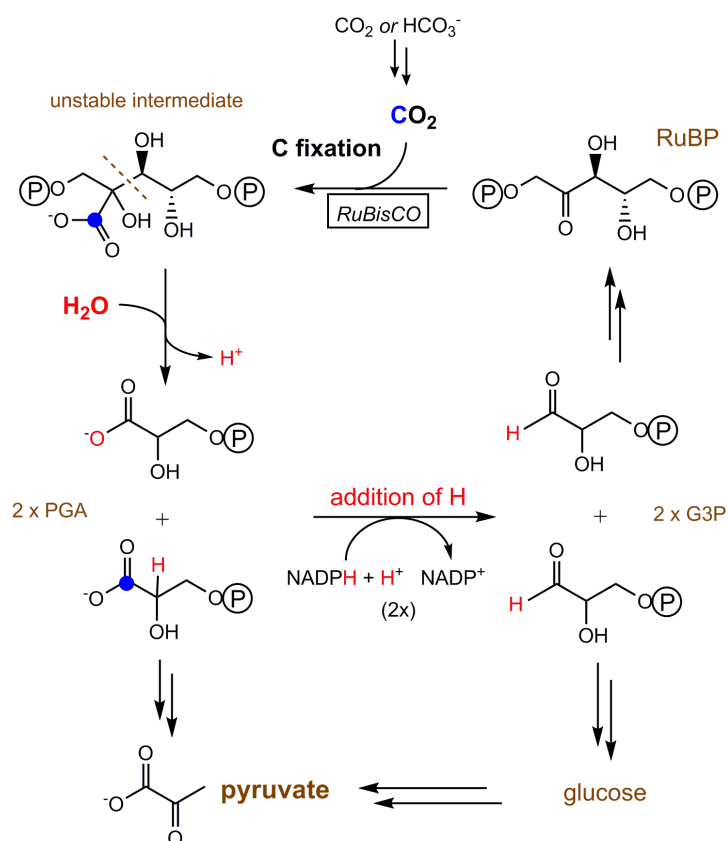
### 2.3 Isotopic fractionation: from substrate to compound

The basics of isotope fractionation apply to organic compounds biosynthesised by organisms across the phylogenetic tree in virtually every aquatic and terrestrial environment. Responsible for the variable isotopic composition of organic molecules is biochemical processing during biosynthesis, which discriminates against the heavier carbon, hydrogen and oxygen isotopes and lighter nitrogen isotope and results in the more processed molecules being isotopically lighter (i.e. depleted in  $^{13}\text{C}$ ,  $^2\text{H}$ ,  $^{18}\text{O}$ ) or heavier (enriched in  $^{15}\text{N}$ ) compared to less processed molecules. An example for such a process is enzymatic carbon chain elongation, which leads to long-chain *n*-alkyl compounds produced by higher plants being depleted in the heavy carbon and hydrogen isotopes compared to short-chain *n*-alkyl compounds, even within the same plant (Diefendorf and Freimuth, 2017, and references therein). Typically, plants are responsible for a fractionation factor ( $\epsilon$ ) of -10 to -30 ‰ for carbon and -100 to -170 ‰ for hydrogen between substrate and *n*-alkyl compounds (Collister et al. 1994; Chikaraishi et al., 2004; Hou et al., 2007; Sachse et al., 2012; Sessions, 2016). An exception to the general depletion of the heavy isotope in products of enzymatically controlled reactions has been observed in some microbes, with inverse hydrogen isotope fractionation, i.e. enrichment of  $^2\text{H}$ , widely occurring in lipids of aerobic heterotrophs (Zhang et al., 2009; Osburn et al., 2016; Kümmel et al., 2016).

Prior to fractionation during biosynthesis, however, it is the isotopic composition of the substrates providing the key elements for primary production, e.g.,  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{O}$  and  $\text{NO}_3^-$  for photoautotrophs, that determines the baseline isotopic composition of an organic compound, and this is where information on paleoenvironmental conditions can be gained.

Atmospheric  $\text{CO}_2$  is taken up by the vast majority of primary producers through photosynthetic carbon fixation, a process that strongly fractionates against  $^{13}\text{C}$  (e.g. Körner et al., 1991; Diefendorf and Freimuth, 2017). For land plants, water availability is one of the parameters that significantly influences fractionation rates during carbon fixation as it exerts a strong control on plant stomatal conductance, which in turn influences biosynthetic fractionation during photosynthesis. Variability of  $\delta^{13}\text{C}$  values of compounds from higher plants is likely to represent water availability, at least qualitatively, when  $\delta^{13}\text{C}$  values are determined for time intervals when vegetation changes were minimal and where no major shifts in atmospheric  $\text{CO}_2$  took place (Diefendorf and Freimuth, 2017). Interpreting changes in *n*-alkane  $\delta^{13}\text{C}$  values as precipitation indicators has been established as a paleoclimatic tool in certain settings (see Kohn, 2010 and references therein).

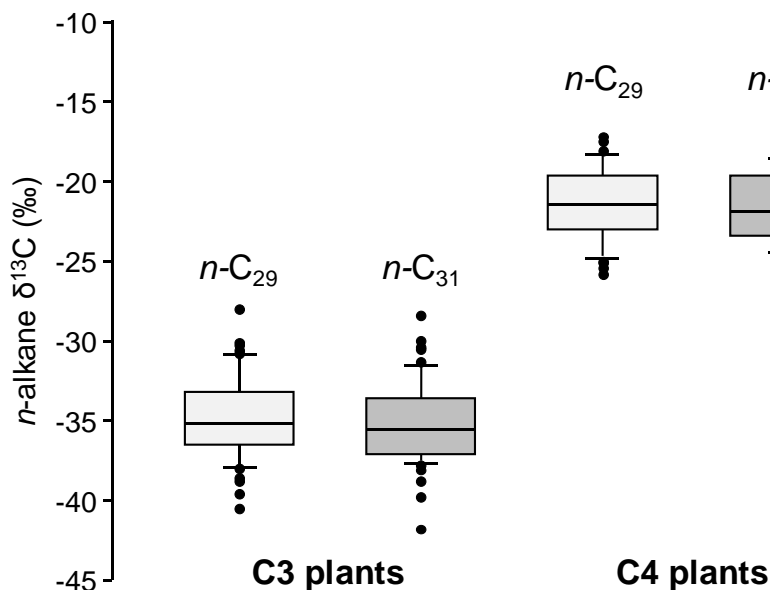




**Figure 1:** Fixation of carbon dioxide through the Calvin cycle during photosynthesis and biosynthesis of pyruvate, the starting material for the biosynthesis of many of the compounds discussed in this review (after Calvin and Benson, 1948; Sachse et al., 2012; Berg et al., 2015). CO<sub>2</sub> and meteoric water are taken up by the photosynthesizing organism for carboxylation and hydrolysis of Ribulose 1,5-bisphosphate (RuBP). This process produces two molecules of 3-phosphoglycerate (PGA) and discriminates against the heavy isotopes (blue dot: added carbon from CO<sub>2</sub>; added hydrogen atoms in red). PGA can be turned into pyruvate either through a 10-step mechanism (not shown) or via the biosynthesis of simple sugars such as glucose (shown on the right), the first step of which is the formation of glyceraldehyde-3-phosphate (G3P). Five out of six G3P molecules produced from three initial RuBP molecules are needed to recover three RuBP molecules while one G3P molecule can be used for the formation of glucose. Thus, six CO<sub>2</sub> molecules are taken up for the formation of one sugar molecule.

Most plants fix carbon directly through the Calvin cycle of photosynthesis (Fig. 1), requiring stomatal gas exchange with the atmosphere for CO<sub>2</sub> uptake in the process, i.e. during daytime. As the first metabolic product contains three carbon atoms (3-phosphoglycerate) these plants are called C3 plants. Under arid conditions, however, some plants fix CO<sub>2</sub> temporarily through the Hatch-Slack pathway by forming oxaloacetate, a molecule containing four carbon atoms, before shifting it into bundle sheath cells where the CO<sub>2</sub> is released to facilitate the Calvin

cycle (for details see Berg et al., 2015). This allows the plants to shift stomatal gas exchange for CO<sub>2</sub> uptake into the night and, thus, minimise water loss. Again, with reference to the first metabolic product, plants following this strategy are called C4 plants. They mainly represent tropical grasses, including maize, for example. Importantly, the C4 metabolic adaption discriminates less strongly against <sup>13</sup>C, leading to a difference in fractionation ( $\Delta^{13}\text{C}$ ) between terrestrial C3 and C4 plants that is significantly greater than 10 ‰, with bulk  $\delta^{13}\text{C}$  values of C3 plants ranging from -22 to -37 ‰ (average of -27 ‰) and of C4 plants from -9 to -15 ‰ (average of -12 ‰; O'Leary, 1988; Kohn, 2010). Therefore,  $\delta^{13}\text{C}$  values of bulk organic matter and individual terrestrial lipids such as leaf wax-derived long-chain *n*-alkyl compounds (see Fig. 2 for *n*-alkane  $\delta^{13}\text{C}$ ) can generally be used to reconstruct spatiotemporal changes in C3 and C4 vegetation, in particular, the relative abundance of tree and shrub-dominated vegetation compared to grasslands (e.g., Huang et al., 2001; Castañeda et al., 2007; Sinninghe Damsté et al., 2011a; Magill et al., 2013; Freeman and Pancost, 2014; Garcin et al., 2014; Johnson et al., 2016). However, apart from the above-mentioned modifying influence of water availability, interspecies differences in isotope fractionation and leaf wax production associated with changes in the plant community will also have to be considered, alongside past variations in the  $\delta^{13}\text{C}$  value of atmospheric CO<sub>2</sub> (Garcin et al., 2014; Diefendorf and Freimuth, 2017).

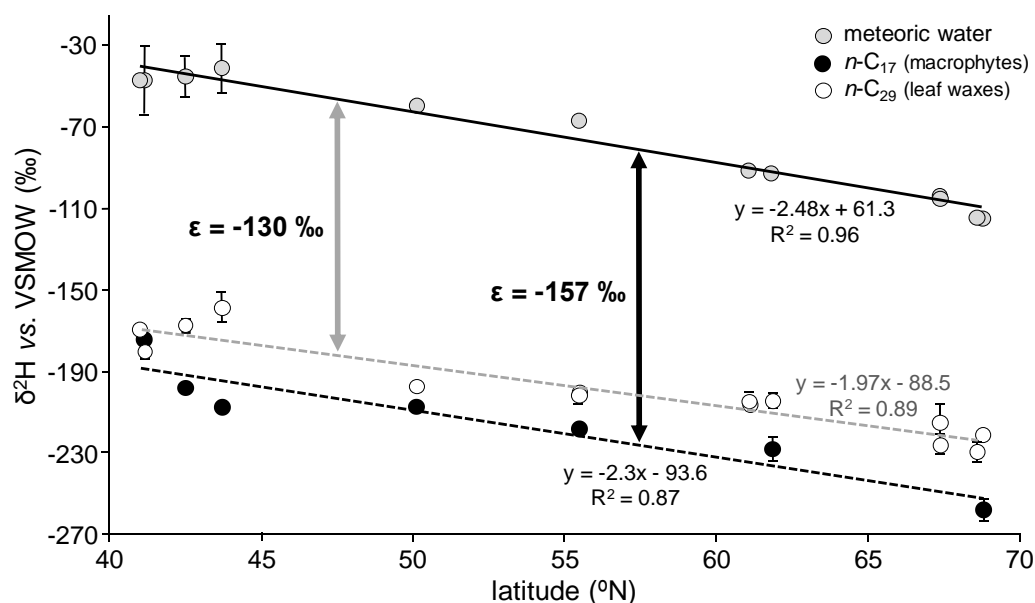


**Figure 2:** Box and whisker diagram of CSI data of plant-wax derived C<sub>29</sub> and C<sub>31</sub> *n*-alkanes of C3 and C4 plants illustrating their potential for reconstructions of vegetation changes in tropical settings (modified from Castañeda and Schouten, 2011, data from Castañeda et al., 2009).

Aquatic primary producers use dissolved carbon dioxide (CO<sub>2[aq]</sub>) or, under CO<sub>2[aq]</sub>-limited conditions, bicarbonate (HCO<sub>3</sub><sup>-</sup>) as inorganic carbon sources for photosynthesis (Lucas, 1983; Prins and Elzenga, 1989). In freshwater lakes, CO<sub>2[aq]</sub> is typically not limited and derives to

variable extent from heterotrophic respiration in the water column or sediment and exchange with the atmosphere (Cole and Prairie, 2009). This means that freshwater photoautotrophs, which are C3 plants, and terrestrial C3 plants partly use the same inorganic carbon substrate, resulting in bulk organic carbon isotope ratios (bulk  $\delta^{13}\text{C}_{\text{org}}$ ) of freshwater algae that are indistinguishable from those of terrestrial C3 plants (Meyers and Teranes, 2001; Lamb et al., 2006 and references therein).

The primary source of hydrogen for biosynthesis in photosynthetic organisms is environmental water, and the major determinant of the  $\delta^2\text{H}$  value of lipids is the  $\delta^2\text{H}$  value of the source water used by the organism (Yapp and Epstein, 1982; Sternberg, 1988; Sessions et al., 1999; Sachse et al., 2012; Rach et al., 2017). Water vapour contained by a specific air mass becomes isotopically depleted in  $^2\text{H}$  as more water precipitates, i.e. with distance from the evaporation centre as well as with cooling and increasing altitude (Craig, 1961; Darling et al., 2005). The basic application of  $\delta^2\text{H}$  values in environmental archives is, therefore, paleohydrology, i.e. the reconstructions of changes in the moisture content of the air mass delivering precipitation or an altogether change in the trajectory and source of the air mass (air mass tracking). Higher plants take up meteoric water (through soil water; Sachse et al., 2012), and evaporation processes during plant respiration (e.g., loss of leaf water) subsequently modify the isotopic composition of the water before it is used in biosynthetic reactions (e.g. Kahmen et al., 2013a, 2013b; Rach et al., 2017).  $\delta^2\text{H}$  values derived from lipids of terrestrial plants will therefore reflect a combined precipitation and evapotranspiration signal (Sachse et al., 2004, 2012). By contrast, submerged aquatic macrophytes and algae use water from the surrounding water column as their hydrogen source. This means that, e.g., in a lake system with no significant fluvial inflow of water from distant areas, the  $\delta^2\text{H}$  values of lipids from submerged macrophytes and algae will mainly reflect the average  $\delta^2\text{H}$  value of local precipitation (Sachse et al., 2004; Fig. 3), unless it is modified by elevated lake water evaporation rates under more arid climate regimes. In this case, the difference between the  $\delta^2\text{H}$  values of macrophyte-derived mid-chain and terrestrial long-chain *n*-alkanes ( $\Delta^2\text{H}$ ) can potentially be used to assess changes in lake water evaporation (Mügler et al., 2008; Aichner et al., 2010a) although this approach still needs further testing (Aichner et al., 2010a; Rao et al., 2014). Nevertheless, many studies have illustrated the generally strong relationship between modern-day climate and  $\delta^2\text{H}$  in lipids in settings with pronounced hydrological gradients (e.g., Huang et al., 2004; Sachse et al., 2004; Nieto-Moreno et al., 2016).



**Figure 3:** Correlation between the  $\delta^2\text{H}$  values of lake water from a European N-S transect and the  $\delta^2\text{H}$  values of the  $\text{C}_{17}$  and  $\text{C}_{29}$   $n$ -alkanes from macrophytes and terrestrial plants in the catchments, illustrating the close control of lake water isotopic composition on leaf wax  $\delta^2\text{H}$  values (modified from Sachse et al., 2004).

The main nitrogen substrates for eukaryotic algae are nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ), while prokaryotic cyanobacteria can directly fix dissolved nitrogen ( $\text{N}_{2(\text{aq})}$ ; Harvey, 1940, 1953; Stal, 2015; Glibert et al., 2016). There is little to no fractionation involved in biological nitrogen fixation (Hoering and Ford, 1960; Minagawa and Wada, 1984), allowing phytoplankton communities dominated by cyanobacteria to be differentiated from eukaryote-dominated communities. As  $\text{N}_2$  can be fixed in both terrestrial and aquatic environments, nitrogen from both of these sources contribute to the lacustrine nitrogen cycle. Isotopic fractionation can occur during many of the transformations nitrogen undergoes, including  $\text{N}_2$  dissolution, nitrification and denitrification, nitrate and ammonium assimilation, and ammonia volatilisation (Collister and Hayes, 1991; Talbot, 2001). Thus, the absolute  $\delta^{15}\text{N}$  value of the substrates provides limited environmental information compared to the absolute  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values of atmospheric and dissolved  $\text{CO}_2$  and meteoric water, respectively. Instead, information on environmental change may be gained from the difference in the isotope values of source amino acids, retaining the isotope composition of the initial substrate, and trophic amino acids, determined by fractionation along each trophic step, with implications for changes in the lacustrine food web structure (see Section 3.2 for details).

The transfer of sulfur between different reservoirs typically involves a change in the oxidation state, which is mediated either through abiologically or biologically induced processes (Strauss, 1997; Farquhar et al., 2000). The main source of sulfur in sediments is derived from

sulfate in the overlying water column or pore waters via downward diffusion in the sediments. Typically, sulfate is reduced to sulfide by bacterial sulfate reduction (BSR), active just below the sediment-water interface, leading to sedimentary sulfide typically depleted with respect to  $^{34}\text{S}$  (e.g., Jørgensen, 1978; Habicht et al., 1998). Isotopic fractionation between sulfate in the water, sulfide, and organic sulfur compounds is fundamentally a function of the availability of sulfate to be reduced and the efficiency of the bacterium present (i.e. large amounts of easily metabolizable organic matter aids the sulfate reduction process; e.g. Kaplan et al., 1963; Canfield and Thamdrup, 1994; Habicht and Canfield, 1997). Favourable conditions for BSR and an open source of sulfate can result in large isotopic fractionation between sulfate and the sulfide product. In the context of restricted settings, such as lakes, sulfate is not readily replenished and may undergo seasonal variation resulting in variations in the range of isotopic fractionation of the sulfate and the product sulfide (i.e. Urban et al., 1999; Zerkle et al., 2010; Oduro et al., 2013, discussed later). Furthermore, the bio-mediated uptake of sulfur into organosulfur compounds in organic matter leads to variable enrichment of  $^{34}\text{S}$  with respect to sulfide phases formed, as well as variability of  $^{34}\text{S}$  across different organic sulfur compounds present (Andreae, 1990; Kharasch, 2013). Typically, studies have focussed on the isotopic variation between original sulfate, the sulfide and bulk organic matter. Utilisation of compound-specific analysis in the examples discussed here is able to better deduce the physical and biochemical processes that lead to sulfur fractionation in sediments.

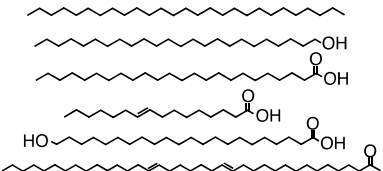
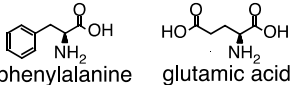
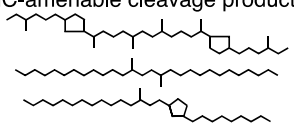

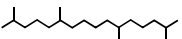
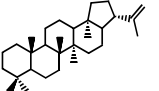
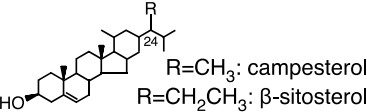

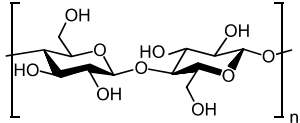
The basic physiological and substrate-related drivers of isotopic fractionation in primary producers during diagenesis are thus relatively well constrained. However, as illustrated by many examples in the remaining sections of this review, a range of environmental and source-specific factors such as temperature, seasonality and salinity or vegetation change and associated changes in evapotranspiration can further modify the isotopic composition of organic compounds. These need to be understood in order to improve the interpretation of CSI data variability in environmental archives. On the other hand, new proxies can be developed that target additional and more specific aspects of ecosystem change, once such causal relationships are established, and it is this improved understanding of isotope fractionation in modern biogeochemical cycles that brings to light the potential of CSIA in future paleoenvironmental studies. The compounds most frequently studied for their CSI values in paleoenvironmental research are alkyl lipids. Therefore, these compounds also provide many examples of the complex relationship between environmental factors, diverse sources and compound-specific carbon and hydrogen isotope ratios, some of which are presented in the following. A more comprehensive introduction to alkyl lipid CSI applications is provided in Section 3.1.

The  $\delta^{13}\text{C}$  values of alkyl lipids are susceptible to more specific and often local factors. Eley et

al. (2016) demonstrate that *n*-alkane  $\delta^{13}\text{C}$  values of C3 and C4 plants from a temperate saltmarsh show a significant variability of  $\delta^{13}\text{C}$  values, with differences between C3 species of up to 10 ‰ and pronounced intra-species differences across the growing season. In a tropical wetland setting, Yamoah et al. (2016) observe large-scale variability in *n*-alkane  $\delta^{13}\text{C}$  values, with long-chain compounds becoming isotopically enriched during drier periods. The authors attribute this finding to a shift in the main substrate from dissolved  $\text{CO}_2$  to isotopically heavier bicarbonate rather than changes in the overlying vegetation and enhanced C4 plant input. Significant differences in the  $\delta^{13}\text{C}$  value between mid- and long-chain compounds have been reported, with the reason behind the offset remaining elusive. An apparently climatically controlled systematic offset of up to 6 ‰ between suberin-derived  $\text{C}_{22}$  *n*-fatty acid and leaf wax-derived long-chain fatty acids in Late Quaternary lake sediments (see supplement to Holtvoeth et al., 2017) could either point to an age-offset between lipids from leaf litter and soils (root material) or to differences in  $\text{CO}_2$  uptake by plants for the formation of leaf and root tissue under variable climatic regimes and different rates of microbial respiration in the soil.  $\text{C}_{22}$   $\omega$ -hydroxy acid found in Miocene lake sediments is reported to be depleted by 4-5 ‰ relative to the long-chain  $\omega$ -hydroxy acids (Huang et al., 1996). In this case, the authors hypothesised this compound to derive from anoxic bacterial biomass. The examples above illustrate the need for an improved understanding of carbon isotope fractionation in natural systems. A detailed review of environmental factors that can influence the  $\delta^{13}\text{C}$  values of fatty acids has recently been published by Reiffarth et al. (2016).

The range of factors that can further modify the  $\delta^2\text{H}$  values of alkyl lipids is even more complex. Additional environmental and physiological variables such as secondary hydrogen exchange reactions and effects of algal growth rates or metabolic differences can influence the isotopic fractionation between hydrogen in environmental water in aquatic and terrestrial lipids (see review by Sachse et al., 2012). Extensive growth experiments have shown that C3 and C4 grasses not only discriminate significantly different against  $^{13}\text{C}$  but also differ in the  $\delta^2\text{H}$  values of their *n*-alkanes by 40 ‰, on average (Gamarra et al., 2016). This could be attributed to the metabolic differences in the way NADPH is produced, i.e. in the bundle sheaths in C4 grasses rather than in the chloroplasts in C3 grasses, with the NADPH then providing the hydrogen for lipid biosynthesis (Gamarra et al., 2016). Studying the leaf wax *n*-alkane hydrogen isotope distribution of riparian trees, Oakes and Hren (2016) describe significant interspecies variation of  $\delta^2\text{H}$  values that can exceed 50 ‰ throughout the growing season. Similarly, Tipple and Pagani (2013) found differences in the correlation between precipitation and *n*-alkane  $\delta^2\text{H}$  values between tree species. However, such interspecies differences appear to be averaged out in the soil as *n*-alkanes from soil samples did show a good correlation between precipitation and CSI  $\delta^2\text{H}$  values. On the other hand, short-term fluctuations in  $\delta^2\text{H}$  of the leaf

wax C<sub>28</sub> *n*-fatty acid reported from the sedimentary record of an Alpine lake may be due to local factors such as length of growing season, amount of snowfall or anthropogenic modification of the local vegetation (Wirth and Sessions, 2016), factors that are not always well constrained. Ladd et al. (2017) investigated the influence of growth rate and temperature on the  $\delta^2\text{H}$  value of algal lipids (fatty acids and brassicasterol) in an oligotrophic and a eutrophic lake. Although the authors found significant variability in the  $\delta^2\text{H}$  values of fatty acids throughout the growing season the average  $\delta^2\text{H}$  value of the C<sub>16</sub> *n*-fatty acid matched the  $\delta^2\text{H}$  value of the lake water and was also preserved in the surface sediment. An in-depth discussion of the factors that can modify  $\delta^2\text{H}$  values of *n*-alkanes exceeds the objectives of our introduction to CSIA and we therefore refer to the very detailed recent review on this matter provided by Sessions (2016).

Compound class	Structures	Application / Indicative for...	Isotope-Proxies	Analytical Technique	Refs.
Alkyl lipids: n-alkanes, n-fatty acids, n-alcohols, unsaturated fatty acids, hydroxy acids, alkenones (structures top to bottom)		meteoric water source / air mass tracking, seasonality, evaporation rates, climate change vegetation change (C3 vs. C4 plants) compound source (terrestrial, aquatic, bacterial) potentially: salinity	$\delta^2\text{H}$ $\delta^{13}\text{C}$ $\delta^2\text{H}, \delta^{13}\text{C}$ $\delta^2\text{H}$	GC-IRMS	1 - 4 5 - 7 4 8 9
Amino acids	 phenylalanine    glutamic acid	food web structure, trophic level compound source	$\delta^{15}\text{N}$ $\delta^{13}\text{C}, \delta^{15}\text{N}$	GC-IRMS	10, 11 12
Glycerol-dibiphytanyl- glycerol tetraethers (GDGTs)	GC-amenable cleavage products* 	terrestrial vs. aquatic sources (brGDGTs, iGDGTs)	$\delta^2\text{H}, \delta^{13}\text{C}$ $\delta^{13}\text{C}$	GC-IRMS SWiM-IRMS	13 - 15 16
Chlorins Maleimides	 maleimide	photic zone euxina source	$\delta^{15}\text{N}$ $\delta^{13}\text{C}$	GC-IRMS	17 18 19, 20
Isoprenoids	 crocetane	paleoenvironment autotrophy vs. heterotrophy	$\delta^2\text{H}$ $\delta^{13}\text{C}$	GC-IRMS	21 22, 23
Hopanoids	 diploptene	bacterial autotrophy vs. heterotrophy methanotrophy	$\delta^{13}\text{C}$	GC-IRMS	24 25
Steroids	 R=CH <sub>3</sub> : campesterol R=CH <sub>2</sub> CH <sub>3</sub> : $\beta$ -sitosterol	meteoric water source, hydrology change, salinity compound source (e.g., terrestrial, aquatic)	$\delta^2\text{H}$ $\delta^{13}\text{C}, \delta^2\text{H}$	GC-IRMS	26, 27 28
Sulfurised compounds	 dibenzothiophene	S cycling in active redox zones pathways of DMS formation VOCS production and release	$\delta^{34}\text{S}$	MC-ICPMS	29 30 31 32
Cellulose		source (terrestrial vs. aquatic) carbon cycling, lake-water balance	$\delta^{18}\text{O}$ $\delta^{13}\text{C}$	GC-IRMS	33 34



**Table 1:** Overview of compound classes, representative structures and isotope applications with key references (reviews where applicable). References are: 1. Sauer et al. (2001); 2. Nichols et al. (2009); 3. Sachse et al. (2012); 4. Sessions (2016); 5. Huang et al. (2001); 6. Sinninghe Damsté et al. (2011a); 7. Garcin et al. (2014); 8. Reiffarth et al. (2016); 9. Schouten et al. (2006); 10. Chikaraichi et al. (2009); 11. Ohkouchi et al. (2017); 12. Larsen et al. (2015); 13. Wuchter et al. (2004); 14. Weijers et al. (2010); 15. Lenggler et al. (2014); 16. Pearson et al. (2016); 17. Boreham et al. (1994); 18. Popp and Hayes (1978); 19. Grice et al. (1996a, 1996b); 20. Wolfe et al. (2001); 21. Grice et al. (2005); 22. Koopmans et al. (1996); 23. Whiteside and Grice (2016); 24. Coolen et al. (2008); 25. Talbot et al. (2014); 26. Sauer et al. (2001); 27. Schwab and Sachs (2011); 28. Chikaraishi et al. (2005); 29. Amrani et al. (2013); 30. Raven et al. (2014); 31. Oduro et al. (2013); 32. Greenwood et al. (2018); 33. Edwards and McAndrews (1989); 34. Street-Perrot et al. (2018). \*for intact molecules see Figures 9 and 10.

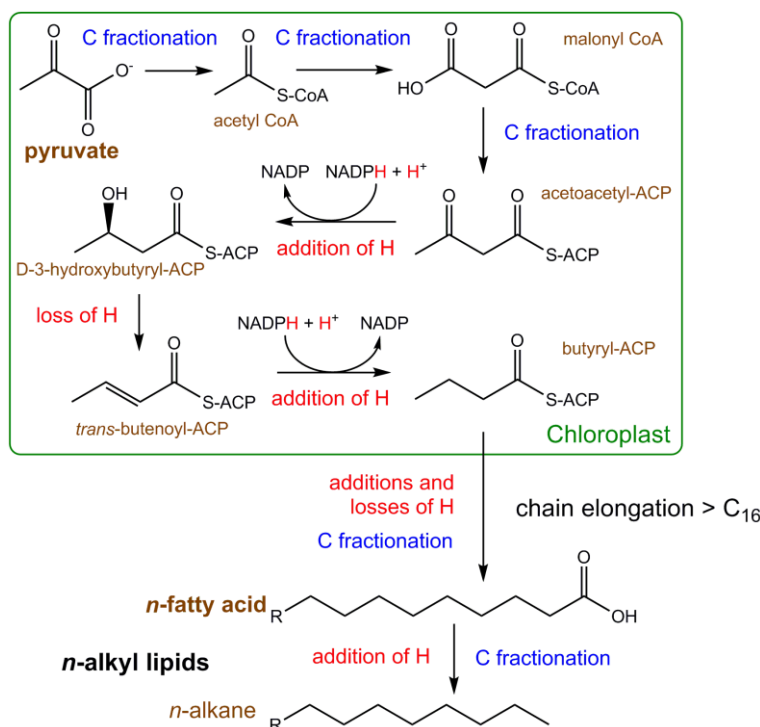
### 3 SOURCES AND CSI APPLICATIONS OF BIOMARKER COMPOUND CLASSES

#### 3.1 Alkyl lipids (*n*-alkanes, *n*-fatty acids, *n*-alcohols, alkenones)

Alkyl lipids of variable carbon chain lengths are ubiquitous building blocks in the formation of organic tissue. They form the hydrophobic part of cell membrane lipids in bacterial, plant and animal tissue (e.g., phospholipids, glycolipids, sphingolipids), function as storage fats (triacylglycerides, steryl esters) or contribute to protective layers such as the wax ester and cutin layers on the outer surfaces of plant cells, mainly on leaves, or suberin on the inside of plant cells, mainly in roots. This wide functional range of alkyl lipids involves different levels of biosynthetic processing, an understanding of which greatly improves the interpretation of CSI values from the various compounds found in a TLE. It also increases the range of paleo-environmental information to be gained, and we therefore briefly introduce the basics of alkyl lipid biosynthesis in the following.

All alkyl lipids produced by primary producers, i.e. mainly photosynthesizing organisms, are based on *de novo* biosynthesis of fatty acids and formed using environmental water and either atmospheric CO<sub>2</sub> or, in case of aquatic organisms, dissolved CO<sub>2</sub> and bicarbonate (HCO<sub>3</sub><sup>-</sup>) as sources for hydrogen and carbon, respectively. Fatty acid biosynthesis follows the acetogenic pathway, using pyruvate derived from the breakdown of sugars (e.g., glucose) to first form an acetyl molecule bound to the co-enzyme A (acetyl CoA), then combining it with malonyl CoA to form a 4-carbon unit (acetoacetyl-ACP), with the reducing agent nicotinamide adenine dinucleotide phosphate (NADPH) replacing an oxygen atom by a hydrogen atom (Fig. 4). Repeated reactions with malonyl CoA and NADPH extend the molecule by two CH<sub>2</sub> units at each step. This process typically ends with the formation of C<sub>16</sub> and C<sub>18</sub> fatty acids and results

in a characteristic dominance of even over odd fatty acid chain lengths in most organisms (for further details on fatty acid biosynthesis see, e.g., Sachse et al., 2012).



**Figure 4:** The “acetogenic pathway” of fatty acid biosynthesis, using pyruvate produced through the Calvin-Benson cycle after CO<sub>2</sub> uptake. Addition and loss of C or H during reactions as well as reactions between molecules discriminate against <sup>13</sup>C and <sup>2</sup>H, i.e. fractionation occurs at each of these steps; ACP = acetyl carrier protein, CoA = co-enzyme A, NADPH = nicotinamide adenine dinucleotide phosphate (partial scheme modified from Sachse et al., 2012).

The C<sub>16</sub> and C<sub>18</sub> *n*-fatty acids, also known as palmitic and stearic acid, respectively, are basic building blocks for a vast range of molecular structures, in particular, membranes. They are modified according to specific requirements such as membrane fluidity through further enzymatic processing, inserting, e.g., double bonds into the carbon chain (unsaturated fatty acids), adding alkyl branches or further functional groups (branched fatty acids, hydroxy acids) or forming cyclopropane units (cyclopropane fatty acids). Higher plants apply further enzymatic processing in epidermal cells to extend the chain lengths of palmitic or stearic acid for the formation of hydrophobic epicuticular wax esters and biopolyesters such as cutin and suberin in the protective layers of leaves and roots (Millar and Kunst, 1997). The activity of fatty acid elongase adds two CH<sub>2</sub> units to the starting molecule (C<sub>16</sub>, C<sub>18</sub> *n*-fatty acid) at each step, resulting again in the dominance of even- over odd-numbered fatty acid chain lengths in plant biomass. *n*-Alcohols and *n*-alkanes are formed through stepwise enzymatic reduction and decarboxylation of *n*-fatty acids (e.g., Coursolle et al., 2015). Because of the removal of

an aldehyde (-CHO) *n*-alkanes are one carbon atom shorter than the original fatty acid, leading to a strong odd over even dominance among *n*-alkanes. Several calcifying and non-calcifying marine and lacustrine haptophytes produce long-chain alkenones, with chain lengths of 37 to 40 carbon atoms and 2 to 4 double bonds, using the same chain-elongating process as land plants initially, followed by desaturation steps (Rontani et al., 2006), during which first di- and then tri-unsaturated alkenones are formed (Kitamura et al., 2018) as opposed to all double bonds being formed at once.

### **3.1.1 Sources**

#### **3.1.1.1. *n*-Alkanes, *n*-fatty acids, *n*-alcohols**

Generally, individual *n*-alkyl lipids are not species-specific. However, as different groups of organisms produce different types of homologous series of alkyl lipids, peaking at different chain lengths, shifts in chain-length distributions observed in a sedimentary archive can point towards changes in the major lipid sources and, hence, towards ecosystem adaption to environmental change. Long-chain *n*-alkyl lipids ( $> C_{24}$ ) are almost exclusively produced by land plants as part of the cuticular wax layer that protects leaves from disease and ultraviolet light, and functions as a barrier to inhibit water loss (e.g., Eglinton and Hamilton, 1967; Volkman et al., 1998; Jetter et al., 2000; Diefendorf and Freimuth 2017 and references therein). Although lower concentrations of these compounds also occur in waxes on the surface of other parts of plants, leaf waxes are commonly assumed to be the dominant source of long-chain *n*-alkyl lipids delivered to lake sediments (e.g., Gamarra and Kahmen, 2015; Diefendorf and Freimuth, 2017). By contrast, alkyl lipids produced by bacteria and aquatic taxa are mainly membrane lipids or storage fats and are dominated by the short-chain compounds, typically by  $C_{16}$  and  $C_{18}$  fatty acids as well as alcohols. Storage fats frequently include unsaturated compounds with chain lengths up to 20 or 22 carbon atoms, such as the essential poly-unsaturated fatty acids eicosapentaenoic acid (EPA) and docosahexaenoic (DHA). However, these biologically highly desirable and labile compounds are usually not preserved in sedimentary records. *n*-Alkanes in aquatic algae and bacteria are dominated by the  $C_{17}$  or  $C_{19}$  homologues (e.g., Gelpi et al., 1970; Sachse and Sachs, 2008) while some macrophytes tend to produce a mid-chain range of *n*-alkanes ( $C_{21}$  -  $C_{25}$ ; e.g., Ficken et al., 2000; Aichner et al., 2010b). Depending on the investigated setting, a fairly robust marker for the supply of *n*-alkanes from peat moss (*Sphagnum* spp.) is the  $C_{23}$  *n*-alkane (see review on *n*-alkane distributions by Bush and McInerney, 2013), although root material of some sedges can be another wetland-related source (Ronkainen et al., 2013). Mid-chain alkyl compounds ( $C_{22}$  and  $C_{24}$  *n*-fatty acids, hydroxy acids, diacids and *n*-alcohols) characterize the alkyl fraction of suberin, an important biopolyester in root material (Molina et al., 2006, Pollard et al., 2008). They can thus indicate soil organic matter supply (Holtvoeth et al., 2016, 2017). Next to

differences in *n*-alkyl chain lengths between species, there are also differences in the overall amounts of plant wax that are produced by land plants. Van den Bos et al. (2018), for example, showed that the concentration of the most abundant *n*-alkane homologues in *Betula pendula* (birch) exceeded 100 µg/g dry leaf material, whereas *Quercus robur* (oak) contained concentrations of around 10 µg/g per homologue or less. Diefendorf et al. (2011) and Diefendorf and Freimuth (2017) show that conifers typically produce significantly smaller amounts of *n*-alkanes than broad-leaved species.

#### 3.1.1.2. *n*-Alkenes

Occasionally, mid-chain mono-unsaturated alkenes maximising at C<sub>25</sub> and C<sub>27</sub> are preserved in lake sediments (Jaffé et al., 1996; van Bree et al., 2014). Investigating their origin, van Bree et al. (2014) found these compounds in sinking particles collected in a shallow sediment trap in Lake Challa, but they were absent in terrestrial organic matter sources in the catchment, which suggests an origin in the oxygenated water column of the lake. Analysing the carbon isotope composition of the C<sub>25:1</sub> and C<sub>27:1</sub> *n*-alkenes, van Bree et al. (2014) were able to confirm an aquatic origin for these compounds as their δ<sup>13</sup>C values were consistent with the expected range for algal biomass in Lake Challa. However, the exact source of the mid-chain *n*-alkenes still has to be identified.

#### 3.1.1.3 Long-chain alkenones

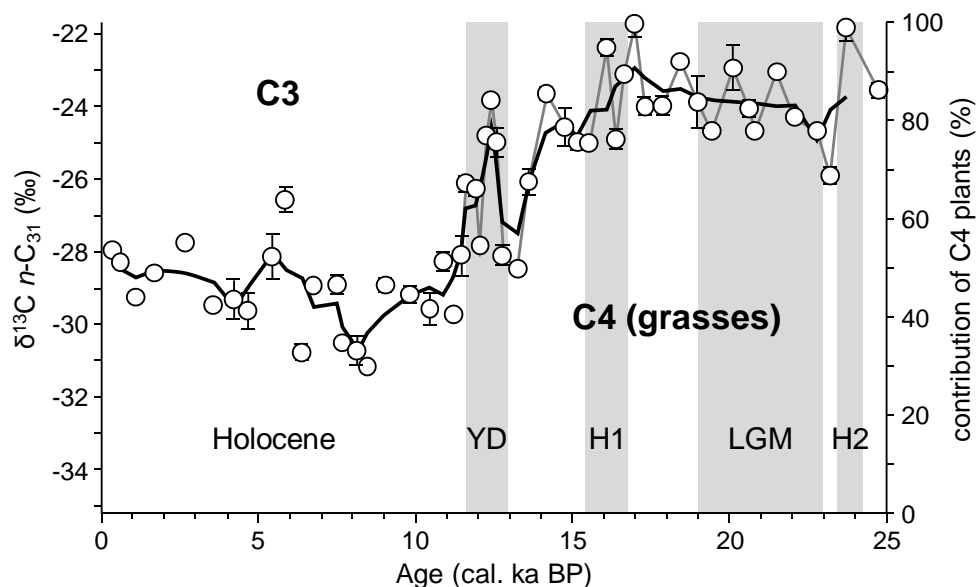
Long-chain alkenones are produced by several calcifying and non-calcifying haptophyte species in marine and saline lacustrine environments (Volkman et al., 1980a,b; Marlowe et al., 1984; Li et al., 1996; Thiel et al., 1997) and serve as energy storage lipids in these algae (e.g., Eltgroth et al., 2005). They have also been found in freshwater systems (Cranwell, 1985; Zink et al., 2001). However, in contrast to marine settings, the source of alkenones in lakes is generally not well defined as lacustrine haptophyte species show great biodiversity that significantly varies between lakes (Theroux et al., 2010; Toney et al., 2010). One of the non-calcifying haptophyte species found in saline lakes is *Chrysotila lamellosa* (Sun et al., 2007) while other alkenone producers appear genetically related to the coastal species *Isochrysis galbana* (Coolen et al., 2004a; D'Andrea et al., 2006; Theroux et al., 2010). For freshwater systems, Zink et al. (2001) speculate that also other, not yet identified non-haptophyte algae may produce alkenones. Nevertheless, alkenones can be abundant alkyl lipids in lake sediments (e.g., Zink et al., 2001; D'Andrea and Huang, 2005; Toney et al., 2011), they are relatively resistant towards diagenetic degradation (Sikes et al., 1991; Prahl et al. 2000, 2003; Freitas et al., 2017) and can thus be targeted as an algal biomarker by CSIA.

#### 3.1.2 Applications

First and foremost, the isotopic composition of an individual alkyl compound can identify or

confirm its presumed source, with the largest differences in biosynthetic isotope fractionation ( $\epsilon$ ) separating terrestrial and aquatic plant matter sources as well as distinguishing between C3 and C4 plants (review by Castañeda and Schouten, 2011) or pointing to methanotrophic bacterial sources (e.g., Summons et al., 1994). Variability in the isotopic composition of a specific compound over time typically reflects ecosystem response to a wide range of potential environmental drivers, including changes in hydrology, seasonality, temperature, and nutrient supply that affect species distribution and diversity. Accordingly, CSI data are ideally combined with further proxy data to narrow down the key system drivers. For example, palynological data may complement CSI proxy records by identifying changes in plant abundance or diversity that reflect the adaption of the vegetation to changes in hydrology or temperature (e.g., Huang et al., 2006; Tierney et al., 2010).

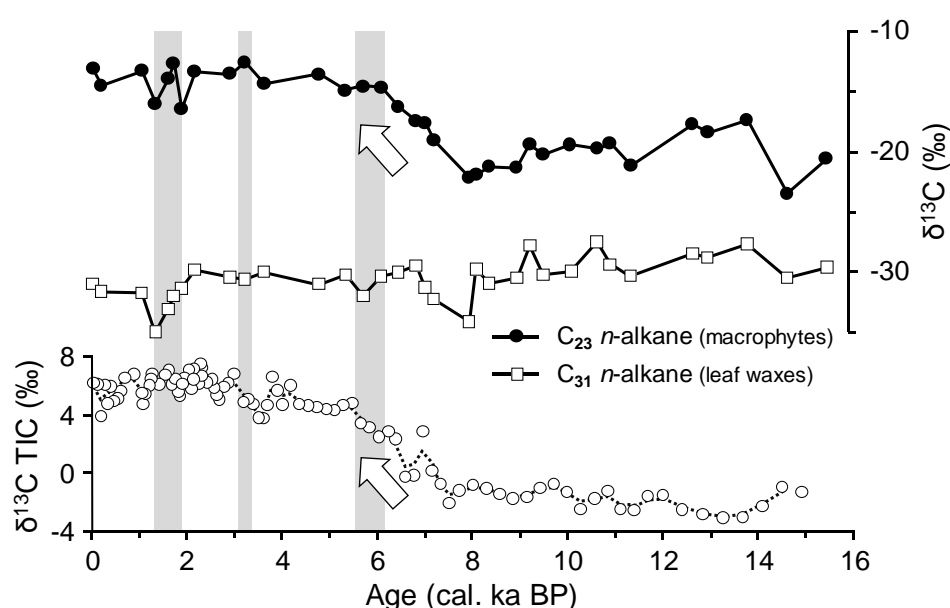
Many studies applying CSIA focus on *n*-alkanes as they are easy to isolate from the TLE, do not require further sample preparation or correction for added carbon or hydrogen during derivatisation and their source is relatively specific, with their main source in sedimentary archives being cuticular plant waxes. Thus, *n*-alkane CSI data interpretation can focus on a limited number of reasonably well understood environmental drivers. For example, Sinninghe Damsté et al. (2011a) used the  $\delta^{13}\text{C}$  values of the  $\text{C}_{31}$  *n*-alkane in sediments of Lake Challa (Mt. Kilimanjaro) to reconstruct glacial-interglacial vegetation change from C4 grass-dominated savannah to C3 vegetation in response to hydrological changes in East Africa over the past 25 ka (Fig. 5).



**Figure 5:** Reconstruction of changing proportions of C3 and C4 vegetation based on  $\delta^{13}\text{C}$  values of the  $\text{C}_{31}$  *n*-alkane in sediments of Lake Challa, East Africa for the past 25 ka, revealing the transition from C4 grass savannah during the last glacial to mixed C3/C4 vegetation in the

Holocene (black line: 3-point moving average, H1/H2 = Heinrich event 1/2, LGM = last glacial maximum, YD = Younger Dryas; modified from Sinninghe Damsté et al., 2011a).

In Lake Koucha on the eastern Tibetan Plateau, Aichner et al. (2010b) found  $\delta^{13}\text{C}$  values of macrophyte-derived  $\text{C}_{23}$  *n*-alkanes (mainly from *Potamogeton*) diverging from the  $\delta^{13}\text{C}$  values of the terrestrial  $\text{C}_{31}$  *n*-alkane but following an equivalent shift towards heavier values in bulk inorganic carbon (TIC)  $\delta^{13}\text{C}$  values, which the authors interpreted as evidence for dissolved  $\text{CO}_2$  limitation due to enhanced productivity at least in the littoral zone of the lake (Fig. 6). This coincided with a shift from a macrophyte-dominated saline ecosystem to a phytoplankton-dominated freshwater ecosystem as indicated by other biomarkers and micropaleontological data.



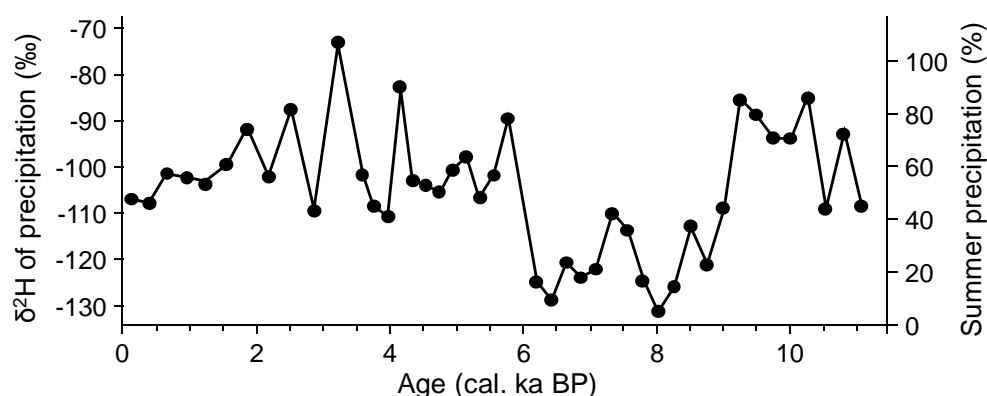
**Figure 6:** CSI data of the  $\text{C}_{23}$  *n*-alkane from macrophytes and the terrestrial  $\text{C}_{31}$  *n*-alkane compared to the  $\delta^{13}\text{C}$  values of bulk TIC in Lake Koucha (eastern Tibetan Plateau), suggesting  $\text{CO}_2$  limitation due to enhanced productivity after 7 cal ka BP (grey bars: cold periods, dashed line: 3-point running average; modified from Aichner et al., 2010b).

The widened scope and an improved understanding of isotope fractionation affecting *n*-alkyl lipids in modern ecosystems has led to a rapid increase in studies targeting a wider range of alkyl lipids for the gain of more specific paleoenvironmental information in recent years. An increasing number of studies apply *n*-alkyl lipid  $\delta^2\text{H}$  values for paleohydrological reconstruction, illustrating the substantial promise of this novel method (Sachse et al., 2012).

Rach et al. (2014) studied the precisely dated varved sediment record from Lake Meerfelder Maar (Germany) to reconstruct changes in hydroclimate over Western Europe at the onset of the Younger Dryas, using *n*-alkane  $\delta^2\text{H}$  values. By comparing the  $\delta^2\text{H}$  records of the terrestrial

$C_{29}$  *n*-alkane and the aquatic  $C_{23}$  *n*-alkane (assumed to derive from macrophytes such as *Potamogeton* sp.) the authors were able to differentiate between the effects of temperature changes, aridification, and moisture source changes and could confirm a 170-year delay between atmospheric cooling in Greenland and hydrology change over Western Europe, which is also backed by palynological data from the site. A later study by Rach et al. (2017) of the Holocene section of the same sedimentary record focussed on the Subboreal-Subatlantic climate transition around 2.8 ka and found terrestrial *n*-alkane  $\delta^2H$  values to confirm the establishment of cooler and wetter conditions, potentially associated with a change in atmospheric trajectories. A sediment record spanning the same time interval obtained from the Netherlands (Engels et al. 2016; van den Bos et al., 2018) shows an opposite  $\delta^2H$ -trend around this time, which could be explained by a change in the atmospheric circulation pattern resembling the negative phase of the North Atlantic Oscillation. Notably, Rach et al. (2017) also observe a large change in  $\delta^2H$  values of aquatic lipid biomarkers ( $C_{21}$  and  $C_{23}$  *n*-alkane) of up to 30 ‰, which the authors assume to result not just from hydrological change but also from ecosystem change as it coincides with a strong increase in aquatic plants and algal remains in the palynological record.

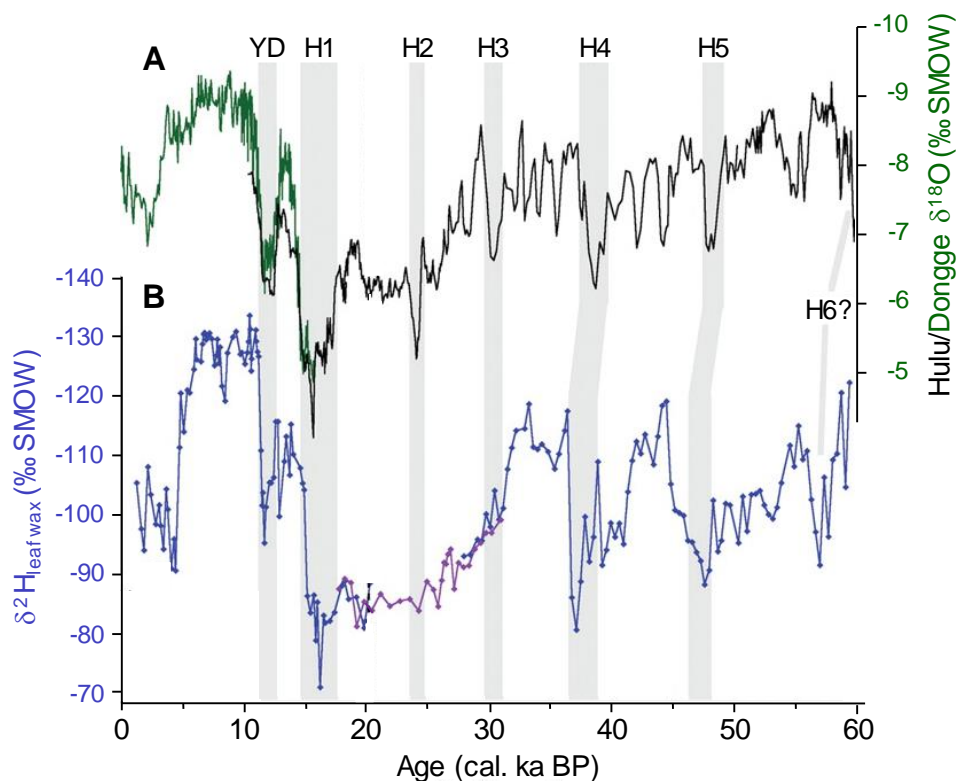
The combination of  $\delta^2H$  and  $\delta^{13}C$  values of the  $C_{29}$  *n*-alkanes in a Norwegian peatland was used to reconstruct Holocene changes in the seasonality of rainfall, one of the more elusive factors determining CSI data outside the monsoon regions (Nichols et al., 2009; Fig. 7).



**Figure 7:** Seasonality of precipitation in NW Norway during the Holocene, expressed as the proportion of summer precipitation and reconstructed from  $n$ - $C_{29}$  alkane  $\delta^2H$  values (modified from Nichols et al., 2009).

Although *n*-alkanes are well established as target compounds for CSIA they frequently are a minor TLE fraction compared to *n*-fatty acids or *n*-alcohols (see, e.g., Cranwell, 1981; Otto and Simpson, 2005; Berke et al., 2012; Holtvoeth et al., 2016), which can provide valuable alternative data when the amount of sample material and extractable *n*-alkanes are too low

for CSIA. Tierney et al. (2008), for example, applied hydrogen isotope ( $\delta^2\text{H}$ ) analysis of the leaf wax-derived  $\text{C}_{28}$  *n*-fatty acid to sediment cores from Lake Tanganyika (East Africa) to reconstruct variations in precipitation patterns over the past 60,000 years in order to better understand the processes that control climate in the tropics. Their data show that this understudied region experienced abrupt paleohydrological changes coeval with orbital and millennial-scale events recorded in Northern Hemisphere monsoonal climate records (Fig. 8). These results provide sound evidence for a strong control of Indian Ocean surface temperatures and winter Indian monsoon on precipitation in southeast Africa.



**Figure 8:** The close correlation of the  $\delta^2\text{H}$  values of leaf wax-derived  $\text{C}_{28}$  *n*-fatty acid in sediments of Lake Tanganyika (B) with the  $\delta^{18}\text{O}$  records of the Hulu and Dongge caves (A) reveal the close linkage between Northern Hemisphere monsoon variability and East African hydrology over the past 60,000 years (YD = Younger Dryas, H1-6 = Heinrich events 1-6; modified from Tierney et al., 2008).

A study by Berke et al. (2012) on sediments of the past 14 kyrs from Lake Victoria combines  $\delta^{13}\text{C}$  data of the  $\text{C}_{29}$  *n*-alkane and, due to the relatively low abundance of *n*-alkanes,  $\delta^2\text{H}$  data of the  $\text{C}_{28}$  *n*-fatty acid with a biomarker-based temperature proxy ( $\text{TEX}_{86}$ ; Section 3.3) in order to reconstruct hydrologically controlled changes in the catchment, in particular, changes in the proportion of C3 and C4 plants. The data are then compared to equivalent data from other African settings, specifically,  $\delta^2\text{H}$  data of the  $\text{C}_{28}$  *n*-fatty acid from Lakes Challa (Tierney et al.,



2011), Tanganyika (Tierney et al., 2008) and Malawi (Konecky et al., 2011) and of the C<sub>29</sub> *n*-alkane from higher plants of the Congo Basin (Scheffuß et al., 2005) and the Zambezi River catchment (Scheffuß et al., 2011). Berke et al. (2012) find their reconstruction in good agreement with other African records and illustrated the spatiotemporal propagation of drier and cooler conditions across East and North Africa after a warm and humid early Holocene as well as the influence of monsoonal moisture supply in periods of maximum seasonal contrast between Northern and Southern Hemisphere insolation. Notably, the authors observe a mismatch between their *n*-alkane  $\delta^{13}\text{C}$  values and palynological data which they attribute to different source vegetation for leaf waxes and pollen from around the lake, underscoring the value of multiproxy approaches. The  $\delta^2\text{H}$  values of the *n*-fatty acids, on the other hand, should be independent of this as they are determined by the  $\delta^2\text{H}$  value of meteoric water rather than interspecies differences in biosynthetic processing. Accordingly, the  $\delta^2\text{H}$  values of the *n*-fatty acids do indeed appear coherent with the changes in the amount of precipitation and associated biome adaption postulated by Berke et al., (2012).

Due to the strong control of meteoric water isotope composition over leaf wax  $\delta^2\text{H}$  values that is particularly pronounced in regions with distinct seasonal changes in moisture source a similar approach was taken by Cisneros-Dozal et al. (2014) for a reconstruction of North American monsoon intensity during the late Pleistocene (540 - 360 ka BP). In the sediments of a paleolake in the southwestern US,  $\delta^2\text{H}$  values of the C<sub>28</sub> *n*-fatty acid reflect the changing intensity of monsoonal moisture supply from the Gulf of Mexico and the Gulf of California, which is seasonally alternating with moisture supply from the cooler North Pacific Ocean. The CSI data resolves the orbitally controlled monsoon variability during interglacials, specifically, during marine isotope stage 11, and thus provides the mechanism driving equivalent changes in pollen, bulk  $\delta^{13}\text{C}$  and GDGT-based temperature data from the same record.

Studying the isotopic composition of *n*-alkyl lipids that are part of tissue types other than cuticular waxes widens the application of CSI data considerably towards aquatic ecosystems as well as towards other terrestrial OM sources such as soil OM (suberin-derived alkyl compounds). In fact, soil OM is the larger carbon reservoir compared to living biomass by a factor of ~2 (Post et al., 1977). The amounts and isotopic composition of suberin-derived  $\alpha,\omega$ -diacids or C<sub>22</sub> and C<sub>24</sub>  $\omega$ -hydroxy acids can provide evidence for the dynamics of the soil carbon pool (Mendez-Millan et al., 2010) ascribed to changes in vegetation cover or land use change and, thus, support established CSIA of leaf wax *n*-alkanes tracking changing proportions of C3 and C4 plants. Even within a pure C3 river catchment, Alewell et al. (2016), for example, were able to distinguish between contributions to river sediment from different OM sources (forest, agricultural land) using CSI data and concentrations of *n*-fatty acids. In order to investigate the links between the isotopic composition of the major limnic carbon

pools, i.e. dissolved inorganic and organic carbon (DIC, DOC),  $\text{CO}_{2(\text{aq})}$ , particulate organic carbon (POC) and algal and bacterial biomass, on the one hand, and lake water  $p\text{CO}_2$ , food web structure and nutrient regime in lakes of different trophic status, on the other hand, de Kluijver et al. (2014) combined bulk substrate isotope values with CSI data of algal and bacterial fatty acids and glucose. This approach revealed complex interdependencies between carbon pool dynamics and isotope values, with nutrient level being a major factor. In order to assess aerobic methanotrophic bacterial production that is responsible for relatively low methane outgassing in Lake Kivu, Morana et al. (2015) interpreted  $\delta^{13}\text{C}$  values of *n*-fatty acids, mono-unsaturated and branched fatty acids alongside  $\delta^{13}\text{C}$  values of methane, DIC and POC from water column profiles. Studying methane production in and outgassing from surface sediments of West, Central and North European lakes, Stötter et al. (2018) found correlations between in-lake methane concentrations and the relative abundance of  $^{13}\text{C}$ -depleted mono-unsaturated fatty acids in the sediments that appeared to derive mainly from methane-oxidising bacteria. However, the authors also find that oxygen availability at the sediment-water interface is a major factor affecting the abundance of these compounds. Thus, although reconstructing changes in methane outgassing from lakes would contribute significantly to the understanding of methane cycling in the past, the extension of such approaches into the paleorecord remains a challenge. Glucose has a low preservation potential, for example, and disentangling the sources of microbial biomarkers from communities living in the water column or *in situ* will be an issue. However, in any such attempt, CSIA will provide an essential tool due to the strong fractionation resulting from the consumption of microbial methane, whichever biomarker from a methanotrophic organism one would be studying. We would like to point out the research opportunities that follow from the relations described above between environmental factors and the isotope composition of certain lipids and glucose in soils and modern aquatic ecosystems since the potential of many of these relations for paleoenvironmental proxy development has yet to be explored.

CSIA of long-chain alkenones from incubation experiments with the dominant marine haptophyte species, *Emiliania huxleyi* and *Gephyrocapsa oceanica*, and the coastal species *Isochrysis galbana* demonstrated that the  $\delta^2\text{H}$  value of the alkenones is generally determined by the  $\delta^2\text{H}$  value of the water and, to a significant extent, by salinity (e.g., Englebrecht and Sachs, 2005; Schouten et al., 2006; M'boule et al., 2014; Weiss et al., 2017). Haptophyte growth rate is another modifying factor (Schouten et al., 2006; M'boule et al., 2014). The concept of alkenone  $\delta^2\text{H}$  values tracking salinity was applied, e.g., by van der Meer et al. (2007) to sedimentary alkenones in the eastern Mediterranean where the alkenone  $\delta^2\text{H}$  value strongly correlates with enhanced freshwater supply during sapropel formation. In a Holocene sediment core from an estuarine site on the west coast of Florida, alkenone  $\delta^2\text{H}$  values also

appear to have varied to some extent with salinity (van Soelen et al., 2014), however, such relation was not seen, e.g., in alkenones in suspended particles and surface sediment from the Chesapeake Bay estuary on the east coast of the US (Schwab and Sachs, 2011). A shift in haptophyte species distribution along with change in salinity is one of the likely reasons for the weak or absent correlation between alkenone  $\delta^2\text{H}$  values and salinity in brackish coastal settings. In North American saline lakes, Nelson and Sachs (2014) observe a correlation, particularly, of the  $\delta^2\text{H}$  value of the  $\text{C}_{37:4}$  alkenone in the surface sediment with lake water  $\delta^2\text{H}$ , although this appears weaker than in the marine realm. As far as we are aware at the time of writing, the applicability of alkenone  $\delta^2\text{H}$  for reconstructions of salinity changes in a lacustrine setting has yet to be tested, ideally, for an extant lacustrine environmental archive where the evolution of both salinity and algal species can also be determined by other means.

Schouten et al. (2001) and D'Andrea and Huang (2005) determined the  $\delta^{13}\text{C}$  values of alkenones in sediments of Antarctic and Arctic saline lakes and found further  $^{13}\text{C}$  depletion in the alkenones relative to other biomarkers such as fatty acids, sterols and steranes, with  $\delta^{13}\text{C}$  values of the alkenones of -35 ‰ (Schouten et al., 2001) to -42 ‰ (D'Andrea and Huang, 2005). These offsets are not straightforwardly explained and low growth rates and high concentrations of dissolved  $\text{CO}_2$  due to the low water temperatures in the investigated settings remain hypothetical causes for enhanced fractionation during alkenone biosynthesis. D'Andrea and Huang (2005) again refer to the uncertain source of the alkenones in Arctic lakes but point out the possibility that the isotopic fingerprint of the alkenones may relate to specific ecological conditions. Similarly, a 1 ‰ shift in alkenone  $\delta^{13}\text{C}$  values in mid-Holocene sediments from a restricted estuary (Charlotte Harbour, Florida) may also derive from a shift in species distribution and an associated change in fractionation as isotopic change in DIC could be ruled out based on  $\delta^{13}\text{C}$  values of carbon from foraminifera (van Soelen et al., 2014). We are currently not aware of CSIA of alkenones in pure freshwater systems, for which the potential of such application for paleoenvironmental reconstructions remains to be explored.

## **3.2 Amino acids**

### **3.2.1 Sources**

Amino acids are biologically ubiquitous compounds present in all organisms, both in the form of proteins (polypeptides, i.e. chains of amino acids) and as precursors and intermediates in the biosynthesis of other essential biomolecules, such as porphyrins, neurotransmitters in animals, and lignin in plants. Heterotrophic organisms typically cannot biosynthesise all amino acids they require, i.e. some amino acids have to be assimilated through food sources. These are known as essential amino acids or source amino acids. By contrast, nonessential amino acids are synthesised by heterotrophs through enzymatically controlled addition of ammonia ( $\text{NH}_3^+$ ) to metabolic intermediates, commonly pyruvate, oxaloacetate,  $\alpha$ -ketoglutarate, in a

process called transamination (for details see, e.g., Lengeler et al., 1999; Chikaraishi et al., 2009). Like many enzymatically controlled biosynthetic reactions, transamination and deamination (removal of ammonia) inherit isotope fractionation (Gaebler et al., 1966) and, in this case, result in  $^{15}\text{N}$  enrichment of the nonessential (or trophic) amino acids (McClelland and Montoya, 2002; Chikaraishi et al., 2007). Thus, the nitrogen isotopic composition of essential and nonessential amino acids in heterotrophic organisms is determined by the source (essential amino acid) and by the level of metabolic processing (nonessential amino acid). Phenylalanine (Phe), for example, is an essential amino acid in mammals and undergoes few metabolic steps in which fractionation could occur, therefore,  $\delta^{15}\text{N}_{\text{Phe}}$  values represent those of the diet, and ultimately the base of the food web. Phe is therefore referred to as a source group amino acid. On the other hand, glutamic acid (Glu) plays a central role in amino acid biosynthesis, and so  $\delta^{15}\text{N}_{\text{Glu}}$  values reflect the amount of N metabolic cycling between the base of the food web and the consumer tissue, and is referred to as a trophic group amino acid (McClelland and Montoya, 2002; O'Connell, 2017).

It is thus possible to estimate the trophic position of organisms in aquatic and terrestrial ecosystems using an equation based on the differing trophic  $^{15}\text{N}$  enrichments of Glu and Phe, of approximately 8 ‰ and 0.4 ‰, respectively (Eq. 2):

$$\text{TL}_{\text{Glu-Phe}} = \frac{\delta^{15}\text{N}_{\text{Glu}} - \delta^{15}\text{N}_{\text{Phe}} - \beta}{7.6} + 1 \quad \text{Equation 2}$$

where  $\beta$  is the difference between Glu and Phe at the base of the food web being studied (Chikaraishi et al., 2009; Chikaraishi et al., 2010; Yamaguchi et al., 2017). This method has benefits over using a bulk method, as the  $\delta^{15}\text{N}$  values of these amino acids provide an internal trophic position measure, without the need to measure the flora and fauna contributing to the diet (Chikaraishi et al., 2007, 2009).

### 3.2.2 Applications

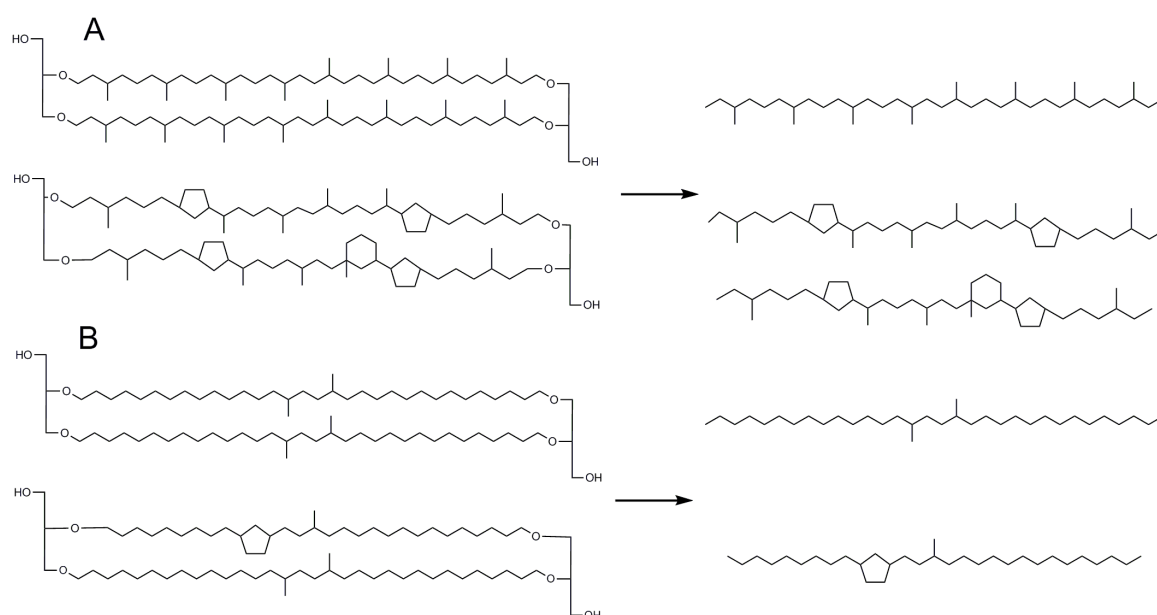
CSIA of amino acids has developed into a tool to improve our understanding of nitrogen transfer in modern aquatic food webs (e.g., Uhle et al., 1997; McClelland and Montoya, 2003; McCarthy et al., 2007; Yamaguchi et al., 2017). An increasing number of studies successfully apply nitrogen as well as carbon CSIA of amino acids to track amino acid production in the limnic water column as well as microbial processing during sinking and in surface sediments (e.g., Carstens et al., 2013). In paleolimnological contexts, the application of CSIA of amino acids has so far been limited due to the relatively low preservation potential of amino acids and the uncertainties associated with nitrogen fractionation affecting individual amino acids during and after entering the sedimentary record. Carstens et al. (2013) observe an early diagenetic decrease of amino acid-bound nitrogen relative to the total nitrogen from 38 to 10

% in the top 6 cm of sediment in two Swiss lakes as well as changes in the  $\delta^{15}\text{N}$  values of amino acids that are also likely to result from *in situ* microbial processing rather than changing inputs over time. Further evidence for heterotrophic alteration of selected amino acids from detrital organic matter leading to a scattered amino acid  $\delta^{15}\text{N}$  pattern is provided in a critical review of amino acid nitrogen CSIA in environmental contexts by Ohkouchi et al. (2017), with the authors concluding that understanding how exactly microbial activity alters amino acid  $\delta^{15}\text{N}$  patterns “remains a frontier area of CSIA-AA applications”. Thus, while amino acid  $\delta^{15}\text{N}$  values may provide information on both organic matter sources and microbial degradation, these processes will have to be understood before any proxy can be reliably applied.

### **3.3 Glycerol-dibiphytanyl-glycerol tetraethers (GDGTs)**

#### **3.3.1 Sources**

Isoprenoidal etherlipids, in particular archaeol and hydroxyarchaeol (diethers) or glycerol dibiphytanyl glycerol tetraether lipids (iGDGTs, Fig. 8A) are the predominant membrane lipids of archaea (Langworthy, 1982, 1977; Langworthy et al., 1972; Schouten et al., 2013). Archaea are widespread in mesophilic settings: marine and lake sediments (MacGregor et al., 1997; Vetriani et al., 1998), soils (Hershberger et al., 1996; Leininger et al., 2006), and the ocean (DeLong, 1992; Fuhrman and Davis, 1997; Karner et al., 2001). Isotopic fractionation has been studied on only a small proportion of cultured organisms (Könneke et al., 2012; van der Meer et al., 2001). The membranes of some bacteria can also consist of diether lipids and tetraether lipids, containing non-isoprenoidal, sometimes methylated, hydrocarbon chains (glycerol dialkyl glycerol tetraetherlipids or branched GDGTs, (brGDGT, Fig. 8B; Sinninghe Damsté et al., 2011b, 2014; Weijers et al., 2006). Sources of brGDGTs comprise microorganisms thriving in lacustrine and riverine environments (Blaga et al., 2010; Tierney and Russell, 2009; De Jonge et al., 2014), peats (Weijers et al., 2006) and soils (Weijers et al., 2007).



**Figure 9:** Glycerol-dibiphytanyl-glycerol tetraether lipids (GDGTs) and cleavage products; A: common isoprenoidal GDGTs (iGDGTs) and biphytanes, B: common branched GDGTs (brGDGTs) and branched and cyclic alkanes (modified from Schouten et al., 1998).

$\delta^{13}\text{C}$  values of GDGTs are most commonly measured after chemical degradation to biphytanes and branched alkanes (Schouten et al., 1998; Fig. 9), but can also be determined for intact molecules by a spooling-wire microcombustion device interfaced with an isotope-ratio mass spectrometer (SWiM-IRMS; Pearson et al., 2016) or possibly by high-temperature GC-IRMS (Lengger et al., 2018). Analytical challenges in the determination of the stable hydrogen isotopic composition are large and only a limited amount of CSI studies focusing on GDGTs have been carried out, so far (e.g., Kaneko et al., 2011).

### 3.3.2 Applications

The applicability of carbon isotopes of GDGTs for lacustrine environmental reconstructions still has to be tested. However,  $\delta^{13}\text{C}$  values of GDGTs have been the subject of a significant number of studies of modern environments that work towards the development of GDGT-based paleoenvironmental proxies. These include stable isotope probing experiments aiming to study origin and metabolism of GDGTs (Wuchter et al., 2003; Lengger et al., 2014), and the determination of natural  $\delta^{13}\text{C}$  values of GDGTs. GDGTs are highly abundant in lakes, and their distributions are well studied as they are used in paleothermometers such as  $\text{TEX}_{86}$  and MBT (Castañeda and Schouten, 2011). Some are produced *in situ* in the lakes, while others are exogenous and derived from surrounding soils or riverine influx. Provided sources and net carbon isotope fractionation factors for archaeal, planktonic iGDGTs such as crenarchaeol are further constrained,  $\delta^{13}\text{C}_{\text{biphytane}}$  could potentially be used as a paleo-DIC proxy in lakes, as suggested for marine settings (Hoefs et al. 1997, Kuypers et al. 2001, Pearson et al. 2016).

Bacterial brGDGTs, on the other hand, have been reported to be depleted by 1 ‰ in  $^{13}\text{C}$  compared to the bulk organic carbon in a peat (Weijers et al., 2010); consistent with a heterotrophic lifestyle. However, in lakes (sediments and water column), brGDGTs were found to be varying with  $\delta^{13}\text{C}$  of POM, but strongly depleted in  $\delta^{13}\text{C}$  in anoxic bottom waters, with values of -43 to -47 ‰ (10 ‰ depleted compared to TOC, Weber et al., 2015) and -42 ‰ (Weber et al., 2018). Weber et al. (2018) attributed this depletion to uptake of  $^{13}\text{C}$ -depleted organic carbon ultimately derived from biogenic methane by the source bacteria living in and below the redox transition under hypoxic and methanotrophic conditions. Thus,  $\delta^{13}\text{C}$  values of brGDGTs in lake sediments can shed light on organic matter sources and lake biogeochemistry.

$\delta^{13}\text{C}$  values of iGDGTs produced by archaea can also be used to study present and past settings of anaerobic oxidation of methane. GDGTs with unusually negative  $\delta^{13}\text{C}$  values have been found mostly in methane seep environments and euxinic water columns, and are strong evidence for anaerobic methanotrophs (ANME; Hinrichs et al., 1999, 2000; Wakeham et al., 2004; Niemann and Elvert, 2008). Recently, these have been used for the first time to trace anaerobic oxidation of methane in sediments of a freshwater wetland (Segarra et al., 2015).

In summary, there are several potential applications for  $\delta^{13}\text{C}$  values of GDGTs as proxies in lacustrine and freshwater environments. These range from establishing the presence of anaerobic methane oxidising archaea, to constraining paleo-DIC and organic matter sources.

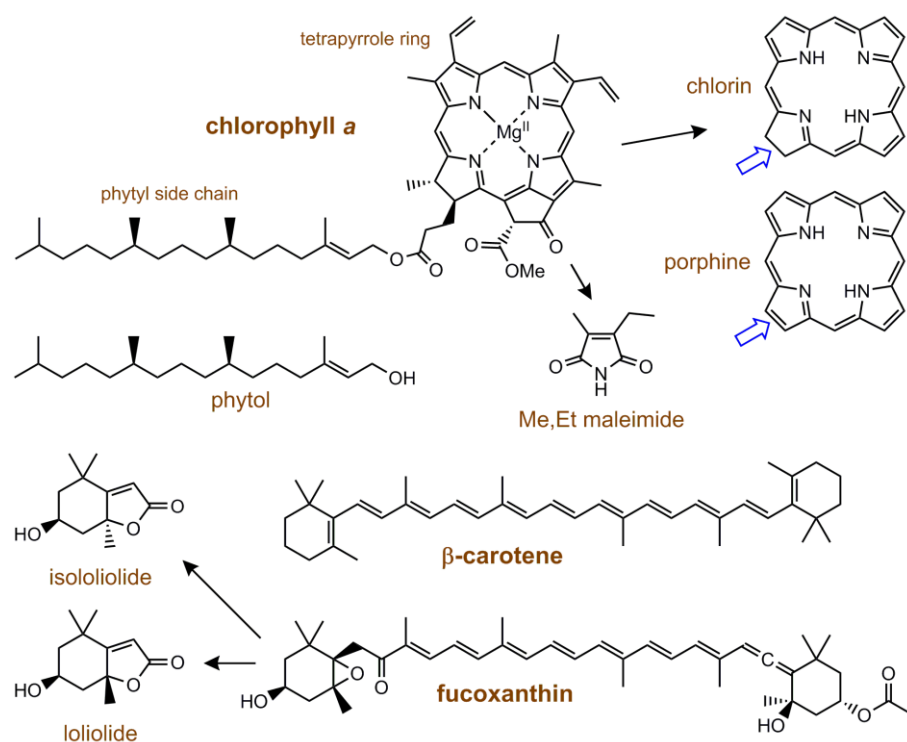
### **3.4 Pigment transformation products**

Key compounds for photosynthesis, chlorophylls and bacteriochlorophylls are the most abundant pigments on the planet. Their transformation products, chlorins, porphyrins, and maleimides can be preserved in lacustrine and marine sediments. Another important group of pigments in plants and microbes are carotenoids. Pigments contain chromophore groups, typically conjugated double bonds that absorb portions of the visible solar spectrum and give molecules their distinctive colours. Many of the pigments integrate oxygen functional groups that provide sites for microbial degradation, making these compounds particularly sensitive to post-depositional alterations. The major forms of stabilizing alterations are complete aromatization of the chlorophyll tetrapyrrole ring to lead to porphyrins and hydrogenation of carotenoids carbon-carbon double bonds to form isoprenoid alkanes (Fig. 10).

The various chlorophylls differ principally in the alkyl sidechains attached to the central tetrapyrrole ring. The most important sidechain of chlorophyll *a*, the most common photosynthetic pigment, is the ester-linked diterpenoid alcohol, phytol (Fig. 10, see Fig. 11 for biosynthesis). As chlorophylls absorb red wavelengths of solar energy, aquatic phototrophs have evolved different carotenoid compounds as accessory pigments to broaden the range of

wavelengths useful for photosynthesis (c.f. Swain, 1985; Sanger, 1988). Many of the accessory pigments are characteristic of different photoautotrophs and this can be used to help identify past sources, synthesis, taphonomy, and freshness of organic matter in limnic records (Naeher et al., 2013).

Chlorophylls undergo minor to major transformations within the water column and in the sediment. These continue during diagenesis and lead to the formation of porphyrins and maleimides (Grice et al., 1996, 1997; Pancost et al., 2002). The reactivity of pigments makes them sensitive indicators of changes in aquatic environments. For example, the diagenetic conversion of chlorophyll to pheophytin is enhanced by acidic conditions, as shown by Guilizzoni et al. (1992) when employed in the reconstruction of the progressive acidification of lakes in the Central Alps.



**Figure 10:** Molecular structures of common pigment types and representative degradation products in limnic settings. Chlorophyll a is the dominant chlorophyll and primary photosynthetic pigment. Secondary pigments such as carotenoids (e.g., β-carotene, fucoxanthin) are present in various amounts in plants and algae as well as dinoflagellates. Pigments are rarely preserved intact whereas degradation products such as chlorin, porphyrins (parent structure: porphine) and maleimides from chlorophylls or loliolide/isololiolide from fucoxanthin are frequently observed in lake sediments and can be used as indicators for photoautotrophs.

### 3.4.1. Chlorins and porphyrins



#### **3.4.1.1 Sources**

Chlorins are broadly defined as chlorophylls and their phaeopigment derivatives central to photosynthesis (Fig. 10) and thus inherently linked to primary producers (Sanger, 1988). As they quickly degrade in light and oxygen, chlorins extracted from water or surface sediments are thought to be derived from synthesis at or close to the collection site, reducing the influence of transport. Degradation of chlorins during diagenesis and transport biases limnic sediments toward autochthonous sources, although chlorins are also synthesized by land plants (Sanger, 1988). Chlorins contain four nitrogen atoms to each molecule (Fig. 10), offering the opportunity for compound-specific  $\delta^{15}\text{N}$  analysis.

Intensively studied since the 1930s (e.g., Treibs, 1936) porphyrins are aromatic organic compounds that consist of carbon and nitrogen and sometimes contain a metal atom such as magnesium at their centre (e.g., chlorophyll). Whereas chlorins comprise the immediate diagenetic products of chlorophylls, geoporphyrins result from long-term diagenesis (cf. Callot et al., 1990). They have vanadium or nickel in their centre and can be preserved in a wide range of sediments for hundreds of millions of years (Eglinton et al., 1985; Callot and Ocampo, 2000).

#### **3.4.1.2 Applications**

The nitrogen isotopic composition of chlorins has been determined from contemporary waters and cultured algae (Sachs and Repeta, 1999; York et al., 2007), as well as from late Quaternary marine and limnic sediments (Sachs and Repeta, 1999; 2000; Higgins et al., 2010), e.g., to provide insights into the marine N-cycle in the Mediterranean sapropel formation. These studies, however, relied upon phaeopigments (Sachs and Repeta, 1999, 2000) or on the coalescence of several chlorin fractions (Higgins et al., 2010). Coupled  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  from chlorins extracted from last glacial-interglacial transition sediments of Lake Suigetsu, Japan (Tyler et al., 2010) emphasize both the potential (e.g., the response of aquatic primary productivity to post-glacial environmental change) and further work needed for chlorin-specific isotopes as tracers in lake sediments.

Where ancient sediments are concerned,  $\delta^{15}\text{N}$  measurements of diagenetic products of chlorins are more prevalent, e.g. metalloalkylporphyrins (Hayes et al., 1987; Ohkouchi et al., 2006 for nitrogen fixation/assimilation) and maleimides (Grice et al., 1996a; Pancost et al., 2002; see Section 3.4.3).

### **3.4.2 Aromatic carotenoids and maleimides**

#### **3.4.2.1 Sources**

Carotenoids are usually yellow- to red-coloured lipids formally derived from the irregular  $\text{C}_{40}$

isoprenoid lycopene carbon skeleton by hydrogenation, dehydrogenation, cyclization and oxidation reactions (Pfenning, 1978). Biosynthesized *de novo* by all photosynthetic bacteria, eukaryotes, halophilic (high salt) archaea, and a large variety of non-photosynthetic organisms, over 600 different carotenoid structures have been identified in modern organisms (Goodwin, 1976; Liaaen-Jensen, 1979; Summons and Powell, 1986). In aquatic sedimentary environments, the only significant biological sources for aromatic carotenoids are green and purple sulfur bacteria, anoxygenic photoautotrophic prokaryotes that inhabit the sulfide-rich, light-limited, and oxygen depleted bottom waters of some lakes and ocean basins (Grice et al., 1996a; Koopmans et al., 1996; Schaeffer et al., 1997).

Maleimides are the oxidation products mainly of the tetrapyrrole nuclei from chlorophyll and/or bacteriochlorophyll related pigments (Fig. 10) and potentially from other sources, e.g., cytochromes (Paoli et al., 2002) and phycobilins from cyanobacteria and rhodophytes (Glazer et al., 1976; Brown et al., 1990), possibly by a transformation pathway involving the oxidation of vinylic chlorophyll substituents and the formation of an aldehyde intermediate during early diagenesis under anoxic conditions (Pickering and Keely, 2011; Naeher et al., 2013). Bacteriochlorophyll (bchl) pigments *c*, *d*, and *e* (1 and 2; M = Mg, R3 = farnesyl) are exclusively made by green sulfur bacteria (Pfennig, 1978).

#### **3.4.2.2. Applications**

Although their multiple double bonds make them reactive compounds that should be interpreted cautiously, source-specific chlorophyll-derived pigments (e.g., carotenoids and maleimides) can be robustly preserved in sediments thousands to millions of years old (as reviewed in Brocks and Summons, 2005), yielding unparalleled information for paleolimnological reconstructions, including details on lake evolution, redox transitions, changing patterns of aquatic primary productivity, and environmental conditions.

The presence of aromatic carotenoids (or bchl derived porphyrins) in lakes provides evidence of anoxygenic photosynthesis in contemporary environments and in sediments, a vast array of diagenetic aromatic components have been identified (Grice et al., 1997; Koopmans et al., 1996) that are derived from green sulfur bacteria (e.g. aromatic compounds isorenieratene/chlorobactene with a 2,3,6 methyl aromatic substitution pattern) or from okenone from purple sulfur bacteria (e.g. with a 2, 3, 4 methyl aromatic substitution pattern; Brocks and Summons, 2005.) These carotenoids and bchl-derived porphyrins serve as a marker for photic zone euxinia in the past. (Grice et al., 1996a,b; Koopmans et al., 1996; Hartgers et al., 1995; Grice et al., 1997; Grice et al., 2005a; Ocampo et al., 1985; Whiteside and Grice, 2016).

Furthermore, changes in primary producers can be inferred from the types of pigments that are present in sediments. For example, progressive eutrophication of Esthwaite Water in the

English Lake District is recorded by increases in the concentrations of the carotenoids indicative of cyanophytes (Griffiths, 1978). Similarly, in other lake settings, relative abundance changes of bchl *a* relative to bchls *c* and *d* indicate development-related changes in the structure of the bacterial community, leading to increased competition for light or nutrients (Abella et al., 1980; Parkin and Brock, 1980; Rodrigo et al., 2000). Differences in the proportions of bchl *e* and bchls *c* and *d* indicate if brown or green species of green sulfur bacteria dominate in lakes of different depths and where different light regimes and chemical conditions prevail (Vila and Abella, 1994). Wilson et al. (2004) looked at the impact of stratigraphic resolution of sediment depth profiles of bchls *c* and *d*, as revealed by methanolysis, in Kirisjes Pond, Antarctica, and a finely laminated microbial mat from Les Salines de la Trinitat, Spain and showed that bacterial communities are highly sensitive to changing conditions and respond quickly. With regard to primary productivity sources on longer timescales, Kimble et al (1974) demonstrated that the major extractable tetraterpane in the ~50 million-year-old lacustrine Green River Formation is the  $\beta$ -carotene derivative perhydro- $\beta$ -carotene, suggesting that algal photosynthesis was the primary source of organic matter to this paleolimnologic system.

A recent modern calibration study for past biogeochemical cycling of redox-stratified lakes by Fulton et al. (2018) observed distinctive  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of pigments and nutrients in the water column and surface sediments of Fayetteville Green Lake (New York, USA), which they attribute to seasonally variable populations of cyanobacteria, purple sulfur bacteria and green sulfur bacteria at the chemocline. Informed by these data, and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values for pyropheophytin and bacteriochlorophyll from the Black Sea deposited during its transition to a redox-stratified basin ~7.8 ka, the authors proposed an isotopic mixing model for nutrient evolution that shows pigment decomposition to a common porphyrin derivative can produce non-specific sedimentary isotope signatures. This model underlines the need for caution and further refinement in paleobiogeochemical interpretations from basins with diverse microbial populations near a shallow chemocline.

Most maleimide studies have looked at the oxidation products of porphyrins in crude oil (e.g., the Quirke et al., 1980 investigation of the Cretaceous Boscan crude oil) and petroleum source rocks (e.g., studies by Grice et al., 1996, 1997 on the Australian Permian Kupferschiefer and Mid-Triassic Serpiano shales that used Me,*n*-Pr and Me,*i*-Bu maleimides and the Me,*i*-Bu/Me,*Et* ratio as indicators for Chlorobi and hence, for the occurrence of photic zone euxinia across the end-Permian extinction). In a recent study, Naeher et al. (2013) linked Me,*i*-Bu maleimide to the presence of photic zone euxinic and anoxic conditions in Swiss lake Rotsee during the last 150 years and throughout the Romanian Black Sea history, including the limnic phase. A further need remains for the detection and characterization of maleimides in recent

lake bodies and sediments to determine their partly unidentified precursors, their formation processes during chlorophyll/bacteriochlorophyll degradation and importance in terms of environmental conditions, particularly the impact of oxygen. In a recent study towards this end, (Naehler et al., 2013) proposed Me,Me and Me,Et indices as novel proxies for estimating the degree of organic matter degradation, which are applicable for longer timescales than e.g. the chlorin index.

Carotenoid and maleimide diagenetic products are easily distinguished by CSIA. For example, bacterially derived green sulfur products are ca. 15 ‰ more enriched in <sup>13</sup>C than phytoplankton biomarkers (e.g., steranes, hopanoids and steroids) due to the assimilation of CO<sub>2</sub> by the reversed TCA cycle (Quandt et al., 1977) rather than the C<sub>3</sub> carbon fixation pathway. Purple sulfur bacteria differ from green sulfur bacteria in that they fix CO<sub>2</sub> by the C<sub>3</sub> pathway and are typically depleted in <sup>13</sup>C due to assimilation of the lighter carbon that characterises the deeper water column (Hollander et al., 1993; Schaeffer et al., 1997).

### **3.4.3 Biomarkers derived from porphyrin pigments**

#### **3.4.3.1 Regular and irregular isoprenoids**

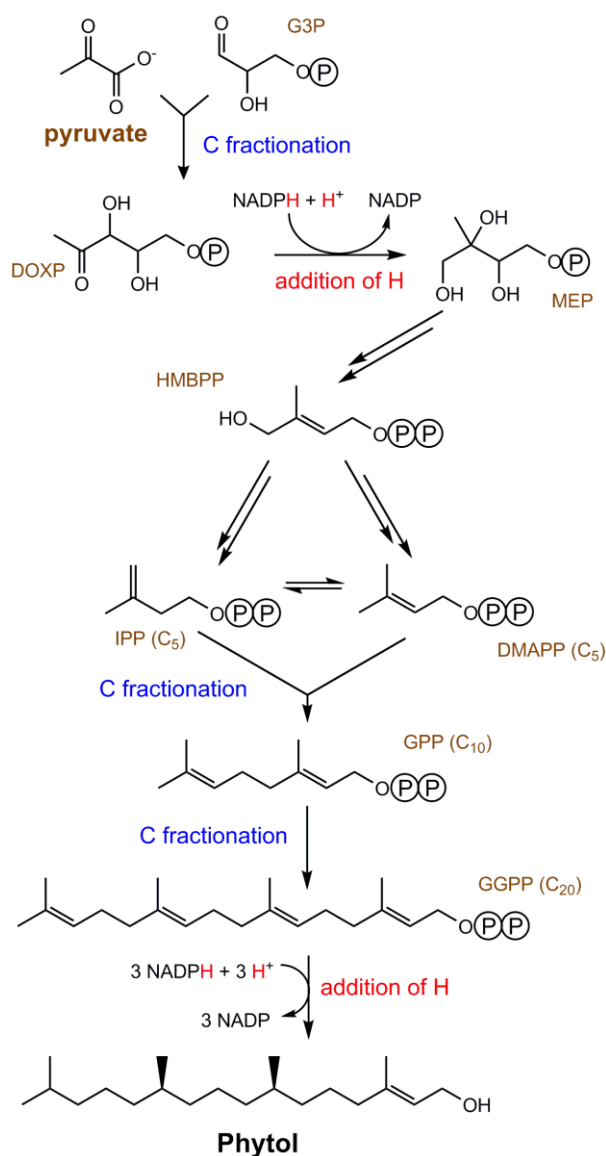
Pristane (Pr) and phytane (Ph), are C<sub>19</sub> and C<sub>20</sub> regular isoprenoid alkanes, respectively, that are largely derived from the phytyl side chain of chlorophyll *a* (Fig. 10, phytol biosynthesis in Fig. 11) in many photosynthetic organisms, as well as from bacteriochlorophylls *a* and *b* of purple sulfur bacteria (Pfenning, 1978). Tocopherols are also precursors of pristane in plants (Goossens et al., 1984). Studies from Dead Sea Basin halites and other hypersaline sediments reveal other sources to be ether-linked membrane lipids of halophiles (Ph) and the C<sub>21</sub> to C<sub>25</sub> regular isoprenoids (Grice et al., 1998). The C<sub>15</sub> regular isoprenoid farnesane is largely derived from the side chain of bacteriochlorophylls *c*, *d*, *e* in green sulfur bacteria (Pfenning, 1978). Other sources for phytane include methanotrophic bacteria (Freeman et al., 1990).

The C<sub>20</sub> irregular isoprenoids crocetane (structure in Table 1) and pentamethylcosane (PMI) have been detected in sediments (e.g., Thiel et al., 1999; Barber et al., 2001; Greenwood and Summons, 2003), modern cultures and microbes (Summons et al., 1996). Crocetane can be a thermally formed product of either archaeal biphytane or isorenieratene from green sulfur bacteria (Maslen et al., 2009). PMI is derived from methanotrophic archaea that live in symbiosis with sulfate-reducing bacteria, allowing the oxidation of methane under strict anoxic conditions (Schouten et al., 1997).

#### **3.4.3.2 Applications**

The δ<sup>13</sup>C of crocetane can reveal whether it stems from a precursor that was biosynthesized by green sulfur bacteria indicative of photic zone euxinia, (values of 11 and -6 ‰) that use the

reverse tricarboxylic acid (TCA) cycle (Summons and Powell, 1986) or by archaea engaging in the anaerobic oxidation of methane (AOM; Orphan et al., 2001; values of -150 ‰). Although  $\delta^{13}\text{C}$  of crocetane has not been measured in Quaternary lake sediment records, a novel study by Tulipani et al. (2015) used relative abundances of methyltrimethyltridecylchromans (MTTCs) and  $\delta^{13}\text{C}$  values with other biomarker parameters as indicators of riverine freshwater incursions (i.e., a freshwater lens) into Middle to Late Devonian paleoreefs (Canning Basin, Western Australia), characterised by prevailing anoxia, persistent photic zone euxinia (Spaak et al., 2018) and water column stratification.



**Figure 11:** The mevalonate-independent pathway (“DOXP/MEP pathway”) for the biosynthesis of phytol via the isoprenoid precursors dimethylallyl pyrophosphate (DMAPP) and isopentenyl diphosphate (IPP), starting with pyruvate produced through the Calvin cycle after CO<sub>2</sub> uptake (Fig. 1); DOXP = 1-deoxy-D-xylulose, G3P = glyceraldehyde-3-phosphate, GPP = geranyldiphosphate, GGPP = geranylgeranyldiphosphate, HMBPP = (E)-4-hydroxy-3-methyl-but-2-enyl pyrophosphate, MEP = 2-methyl-erythroyl-4-phosphate, NADPH = nicotinamide adenine dinucleotide phosphate (after Sachse et al., 2012).

### 3.5 Isoprenoid biomarkers of *Botryococcus braunii*

#### 3.5.1 Sources

Three races of the unicellular green microalga *Botryococcus braunii* are reported (A, B and L), and are characterized by their hydrocarbon lipids. The B race makes C<sub>30</sub> to C<sub>37</sub> branched isoprenoidal hydrocarbons called botryococcenes, giving rise to the isoprenoidal biomarkers

botryococcane (e.g. Maxwell et al., 1968; Metzger and Largeau, 1999; Grice et al., 1998) and a range of cyclic botryococcenes (Metzger et al., 1985) and polymethylated squalenes (Summons et al., 2002). Botryococcane is biosynthesized by the mutual action of separate and distinct squalene synthase enzymes (Niehaus et al., 2011), whereas the L race biosynthesise a C<sub>40</sub> isoprenoid hydrocarbon, lycopa-14(E),18(E)-diene (Grice et al., 1998 and references therein). B-race biomarkers are indicative of freshwater to brackish lakes and saline seas (e.g. Maxwell et al., 1968; Metzger and Largeau, 1999; Grice et al., 1998; Summons et al., 2002) from varying latitudes (Tyson, 1995).

### **3.5.2. Applications.**

Biomarkers derived from *Botryococcus* are more enriched in <sup>13</sup>C compared to other phytoplankton biomarkers in both sediments (Huang et al., 1995; Grice et al., 1998; Huang et al., 1999; Audino et al., 2001; Summons et al., 2002) and culture (Summons et al., 1996). Potential explanations include (1) isotopic fractionation associated with photosynthesis may not be fully expressed due to limiting internal pCO<sub>2</sub> in these microalgae, (2) the thick outer walls may limit the CO<sub>2</sub> diffusion rates, thereby enriching biomass in <sup>13</sup>C (Boreham et al., 1994), and (3) *Botryococcus braunii* utilize a <sup>13</sup>C-rich bicarbonate source (Huang et al., 1999 and references therein). Sediments recovered from the last glacial maximum have *Botryococcus* biomarkers (Huang et al., 1999) that are significantly enriched in <sup>13</sup>C (δ<sup>13</sup>C = 5%). These values are attributed to low atmospheric pCO<sub>2</sub> and accompanying depletion of dissolved CO<sub>2</sub> causing these microalgae to assimilate isotopically heavier bicarbonate from their lacustrine environment. The δ<sup>2</sup>H of lipids (e.g., alkadienes, botryococcenes, heptadecenes, fatty acids, and phytadiene) from *Botryococcus braunii*, closely follow the δ<sup>2</sup>H of the assimilated water (Zhang et al., 2007), and have been used alongside n-alkanes in lacustrine oil shales (torbanites) of Permian to Carboniferous age to disentangle dual-source systems in tropical and glacial environments (Dawson et al., 2004).

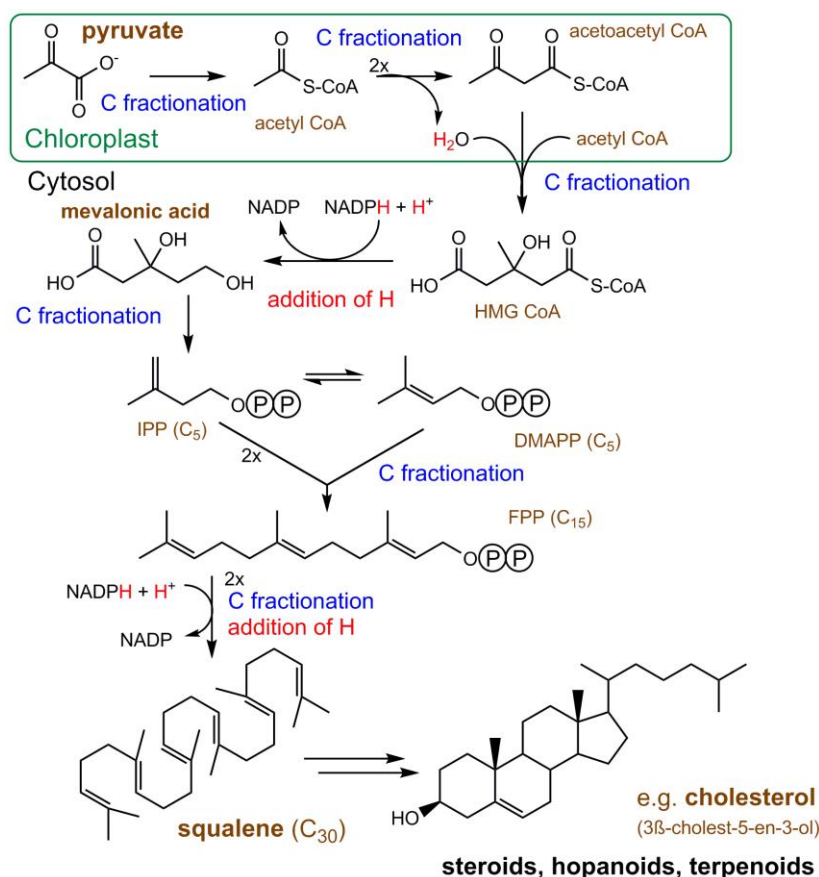
## **3.6 Bacterial hopanes and hopenes**

### **3.6.1 Sources**

Bacterial hopanes and hopenes are a class of pentacyclic triterpenoids that comprise membrane lipids produced by bacteria (Rohmer et al., 1984). Although only about ~10% of bacterial types produce bacteriohopanoids, it is generally not possible to link a given hopanoid to a specific bacterial source (Pearson et al., 2007). The use of compound-specific isotopes, however, offers tremendous power for distinguishing among potential bacterial sources of hopanes and hopenes (Freeman et al., 1990). Hopanoid-producing bacteria in limnic settings include photo- and chemoautotrophs, and heterotrophs able to grow on a wide variety of carbon sources (Freeman, 1990; Pancost and Sinninghe Damsté, 2003; Sessions, 2016). Bacterial hopanoids have long been considered functional analogues of eukaryotic sterols

(Rohmer et al., 1984), although the specifics of their roles in membranes remain the subject of extensive investigation (e.g. Poralla et al., 1984; Welander et al., 2009; Blumenberg et al., 2012; Eickhoff et al., 2013; Ricci et al., 2017).

Bacteria produce hopanoids from squalene via the mevalonic pathway of squalene biosynthesis as shown in Figure 12, starting with pyruvate and followed by cyclization of squalene to form the C<sub>30</sub> compounds 17 $\beta$ ,21 $\beta$ (H)-hop-22(29)-ene (diploptene; Table 1) and diplopterol, and may build upon the diploptene structure via adenosylhopane to synthesize diverse C<sub>35</sub> bacteriohopanepolyols (BHPs, Rohmer, 1993; Bradley et al., 2010). Modifications to the hopanoid structure (methylation at C-2 or C-3, unsaturation within the ring structure, side-chain length and composition) have traditionally been interpreted as indicators of specific bacterial lineages (e.g. Summons et al., 1999; Talbot et al., 2014). However, further research indicates it is increasingly likely that the specific distribution of hopane and BHP structures reflects environmental conditions or metabolic processes rather than, or in addition to, phylogeny (e.g. Ricci et al., 2014; Osborne et al., 2017). Source attribution may yet prove more specific for some compounds (e.g. 35-aminobacteriohopane-30,31,32,33,34-pentol in Type I methanotrophic bacteria; Neunlist and Rohmer, 1985; Talbot et al., 2003; but see van Winden et al., 2012; Rush et al., 2016) or some settings (e.g. hop-17(21)-ene and 2-methylhop-17(21)-ene in methanotrophic *Sphagnum* symbionts; van Winden et al., 2010). Nonetheless, elucidating the relationships between bacterial hopanoid synthesis and environmental conditions will further enhance the information that can be derived from these compounds.



**Figure 12:** The “mevalonic pathway” for the biosynthesis of squalene, starting with pyruvate produced through the Calvin cycle after CO<sub>2</sub> uptake (Fig. 1); CoA = co-enzyme A, DMAPP = dimethylallyl pyrophosphate, FPP = farnesyl pyrophosphate, HMG = 3-hydroxy-3-methylglutaryl, IPP = isopentenyl diphosphate, NADPH = nicotinamide adenine dinucleotide phosphate (after Sachse et al., 2012).

In marine and freshwater nitrogen cycling, anaerobic oxidation of ammonium (anammox) to dinitrogen gas (N<sub>2</sub>) with nitrate as an electron acceptor is an important microbial process performed exclusively by anammox bacteria. A stereoisomer of bacteriohopanetetrol (BHT), BHT II, has been unequivocally identified in culture enrichments of anammox bacteria and oxygen minimum zone waters, microbial hotspots responsible for fixed nitrogen removal (Sáenz et al., 2011; Rush et al., 2014). Given the residence time in geological sediments, the BHT isomer is a potential biomarker for past anammox activity (Matys et al, 2017; and potential expansion of OMZs in warmer worlds of Earth’s deep past), which has heretofore eluded detection through ladderane fatty acid abundances in sediments older than 140 ky (Jaeschke et al., 2009).

Carbon isotopic analysis of hopanes and hopenes is by far the most commonly exploited isotope system for bacterial hopanoids (Pancost and Sinninghe Damsté, 2003). In order to deconvolve bacterial hopane and hopene sources, studies often focus on the stable carbon



isotopic compositions of C<sub>29</sub> to C<sub>31</sub> 17 $\beta$ ,21 $\beta$ (H)-hopanes and hopenes (e.g. Aichner et al., 2010b; Davies et al., 2016; Zheng et al., 2014). Analysis of functionalized hopanols (e.g. diplopterol) can be accomplished through derivatization with BSTFA (e.g. Hollander and Smith, 2001), however a correction must be applied to account for carbon added with the trimethyl silica moiety (Jones et al., 1991). Although  $\delta^2\text{H}$  analyses promise to provide substantial further information (Osburn et al., 2016; Zhang et al., 2009), few environmental studies measuring  $\delta^2\text{H}$  in hopanoids have been conducted to date (Sessions 2016; Li et al., 2009). As the topic of stable hydrogen isotopes in paleoenvironmental research has been thoroughly discussed in a recent review (Sessions, 2016), this section focuses on stable carbon isotopes.

### **3.6.2. Applications**

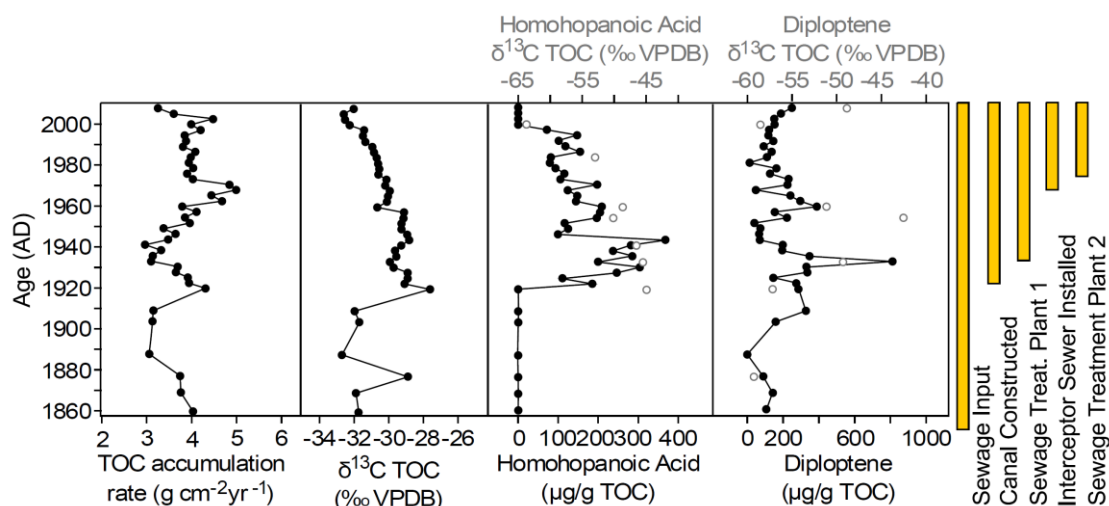
Because carbon source and biosynthetic pathway can have substantial impacts on hopane and hopene carbon isotopic composition, the carbon isotopic composition of hopanes and hopenes is often used to differentiate photoautotrophic and heterotrophic bacterial sources from chemoautotrophic and methanotrophic bacterial sources. This can provide valuable insight into lacustrine carbon cycling, sources of sedimentary organic carbon, cryptic changes in bacterial community composition, and changes in water column structure. For example, Hollander and Smith (2001) demonstrated a striking increase in recycling of carbon associated with the post-1900 AD extreme eutrophication of Lake Mendota through the carbon isotopic composition of hopanol in tandem with other markers of lacustrine primary producers. A similar approach, using compound-specific carbon isotope analyses of hopanes as well as other sedimentary lipids (steranes, pristane, phytane) in the ~50 million year old lacustrine Green River Formation clearly demonstrated protracted meromixis and abundant chemoautotrophic and methanotrophic bacteria (Collister et al., 1992).

Many studies that seek qualitative assessment of intensive methane cycling in wetlands and lakes utilize carbon isotope analyses of hopanes. Incorporation of biogenic methane-derived carbon into bacterial biomass results in hopanes with substantial depletions in  $^{13}\text{C}$  (Summons et al., 1994; Jahnke et al., 1999; but see also Sakata et al., 2008; and Kool et al., 2014). Although absence of  $^{13}\text{C}$ -depletion in hopanes and hopenes is inadequate to exclude methane cycling, the presence of hopanes or hopenes with carbon isotopic compositions of  $< -40\text{‰}$  is often explained as at least a partial contribution from methanotrophic bacteria (e.g., Freeman et al., 1990; Schoell et al., 1994). This is particularly true in wetland deposits where hopanes are more depleted in  $^{13}\text{C}$  than  $\sim -34\text{‰}$  are rarely observed (van Winden et al., 2012; Pancost et al., 2000). For example, in a study of Holocene wetland deposits, Zheng et al. (2014) observed that increased diploptene concentrations with lower  $\delta^{13}\text{C}_{\text{diploptene}}$  (from  $\sim -32\text{‰}$  to  $-42$  to  $-50\text{‰}$  around 6.4 to 4 thousand years ago) coincided with decreased abundances of lipids

derived from methanogens and locally dry conditions. Zheng et al., (2014) attribute this combination of observations to increased efficiency of aerobic methane oxidation and bacterial incorporation of methane-derived carbon under drier conditions. Consequently, drier phases had a two-fold impact on wetland methane emissions through decreased methanogenesis as well as more efficient aerobic methanotrophy. These findings provide a mechanism linking changes in wetland water balance and the Asian monsoon with the mid-Holocene decrease in atmospheric methane concentrations, findings which have been robust to further study over a longer timescale (18kyr; Huang et al., 2018). For glacial-interglacial cycles, Talbot et al. (2014) showed the highest abundance of highly specific BHP biomarkers for aerobic methane oxidation, 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol) from the Congo River Basin correlated with warm intervals. CSIA for BHPs indicate aminopentol was likely supplied by terrestrial watershed or gas hydrates/subsurface reservoirs. This study is a demonstration of the large potential of aminoBHPs to trace and, once better calibrated and understood, quantify past methane sources and fluxes.

In lacustrine settings, methane incorporation into bacterial biomass is greatest in localized areas of diffusive methane flux, rather than plant-mediated or ebullition (Davies et al., 2016). Even so, several studies have effectively documented changes in incorporation of methane derived carbon in hopanoids as a function of climatic conditions (water balance, temperature) or anthropogenic factors (eutrophication). Elvert and colleagues (2016) demonstrate that the Holocene Thermal Maximum is associated with enhanced methane processing in a North American Arctic thermokarst lake. Aichner et al. (2010b), as part of a broad paleolimnologic investigation of Lake Koucha in the eastern Tibetan Plateau, observe an increase in the concentration of  $^{13}\text{C}$ -depleted hopanoids, including diploptene (-45.5 to -62.7 ‰), beginning around 7,000 cal BP. The authors attribute this increase in both bacterial contribution to sedimentary organic matter and incorporation of methane-derived carbon into bacterial biomass to lake freshening. Naeher et al. (2014) utilize the previously determined eutrophication history of Lake Rotsee, Switzerland to examine trends in biomarkers associated with methane cycling. This analysis indicated that increased primary productivity and stratification led to an increase in the concentrations of  $^{13}\text{C}$ -depleted diploptene (-60 to -43 ‰) and homohopanoic acid (-64 to -45 ‰), although the two compounds' concentrations and isotopic compositions exhibit a complex relationship, suggesting a larger role for methane oxidizing bacteria from the 1930s onward in Lake Rotsee (Fig. 13). While some lake hopanoid CSIA datasets indicate active incorporation of methane-derived carbon for long timescales (e.g., Street et al., 2012), this is not the case for all lakes (e.g., Huang et al., 1999; Sarkar et al., 2014).

Despite the insights afforded by CSIA of bacteriohopanoids into relative changes in the intensity of assimilatory methane oxidation, diverse sources of uncertainty and the idiosyncratic natures of lakes and wetlands impede efforts to devise a generalizable or quantitative proxy for assimilatory methane oxidation or methane emissions. Consequently, much additional work remains to be done to refine the use of hopanoid carbon isotopes to assess past changes in limnic carbon cycling.



**Figure 13:** Homohopanoic acid and diploptene reflect changes in methane cycling as a function of anthropogenic impacts on Lake Rotsee, Switzerland (modified from Naeher et al., 2012; 2014). Persistent nutrient inputs associated with sewage inputs, coupled with water balance and sedimentation impacts of canal construction triggered eutrophication and stratification. This increased organic matter supply combined with anoxia drove increases in bacterial productivity (hopanoid concentrations) and incorporation of biogenic methane into bacterial biomass (carbon isotopic composition of hopanoids).

### 3.7 Steroids

#### 3.7.1 Sources

Sterols, the biological precursors of steranes commonly found in sedimentary rocks, are a diverse group of polycyclic isoprenoids (tetracyclic triterpenoids) characteristic of Eukarya (Rohmer et al., 1979; Volkman, 1986). Sterols represent a significant fraction of the lipid pool in marine algae (Jones et al. 1994), and play a key structural role in organisms, including control of cell membrane fluidity, cell signaling, phagocytosis, and stress tolerance (Bloch, 1991; Castoreno et al., 2005; Volkman, 2005). Like hopanoids, sterols are biosynthesized following the same mevalonate pathway that produces the C<sub>30</sub> isoprenoid squalene (Figure 12, section 3.6). Biosynthesis continues with the epoxidation of squalene (C<sub>30</sub>) to oxidosqualene, followed by a subsequent cyclization to two intermediate molecules (protosterols), cycloartenol and lanosterol, respectively (e.g., Volkman, 2005; Summons et al.,

2006). A series of enzymatic oxidation and decarboxylation steps leads to the formation of animal and fungal steroids (e.g., cholesterol [C<sub>27</sub>] and ergosterol [C<sub>28</sub>]) from lanosterol, and the formation of plant sterols (e.g., sitosterol [C<sub>29</sub>]) from cycloartenol. In contrast to hopanoids, the biosynthesis of sterols is oxygen-dependent (e.g., Summons et al., 2006). Although Eukarya are the primary producers of sterols, a limited number of steroid structures have also been reported in a small number of bacteria, including cyanobacteria (e.g., Pearson et al. 2003; Volkman 2003, 2005). A recent study, however, indicates that the potential for bacterial sterol synthesis may occur more widely than previously thought (Wei et al., 2016).

The diversity of sterols is determined by the number of carbon atoms in their skeleton (e.g., C<sub>26-30</sub>), the position of hydroxyl (alcohol) functional groups in the ring system, the position of unsaturations (double bonds) in the ring structure and side chain, and differences in ring and/or side-chain alkylations (e.g., Volkman, 1986; Volkman, 2005). While some sterols can be considered characteristic of a given algal class, many of them are widely distributed and less diagnostic. For instance, 24-norcholesterol (C<sub>26</sub>) has been reported in some diatom and dinoflagellate species (Rampen et al., 2007); cholesterol (C<sub>27</sub>) is typically found in red algae and metazoa (Volkman, 1986, 2003; Volkman et al., 1998; Kodner et al., 2008); 24-methylcholesterol (C<sub>28</sub>) is present in chlorophyll-c containing algae (dinoflagellates, coccolithophores, diatoms) and prasinophytes (Volkman, 1986, 2003; Volkman et al., 1998; Kodner et al., 2008; Rampen et al. 2010); 24-ethylcholesterol (C<sub>29</sub>) is found in green algae, prasinophytes, diatoms and land plants (Volkman, 1986, 2003; Volkman et al., 1994, 1998; Kodner et al., 2008; Rampen et al. 2010); 24-*n*-propyl-cholesterol (C<sub>30</sub>) is present in Chrysophytes and pelagophytes (Moldowan, 1984; Volkman et al., 1998). Additionally, 23,24-dimethyl-cholesterols are present in dinoflagellates and haptophytes, while 4-methylsterols and 4,23,24-trimethylcholesterol (dinosteranes) derive mostly from dinoflagellates (de Leeuw et al., 1983; Summons et al., 1987; Withers 1987; Mansour et al., 1999).

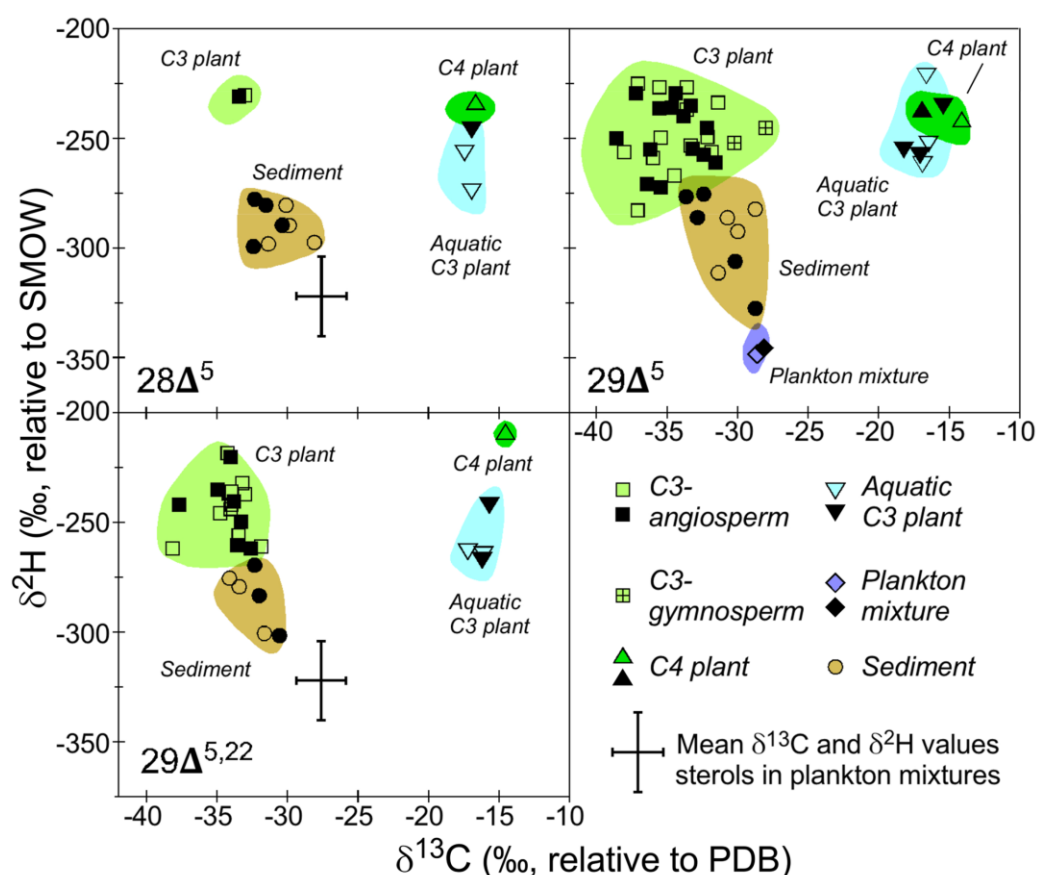
The diagenesis of sterols leads to modifications in their molecular structure as a result of photo oxidation, oxidation, reduction, dehydration, rearrangement, hydrogenation, and aromatization (e.g., Mackenzie et al., 1982; Meyers and Ishiwatari, 1995; Peters et al., 2005). These reactions result in the loss of double bonds and/or hydroxyl groups, and the generation of stanols, stanones, sterenes, and aliphatic and aromatic steranes. Due to their broad diversity, relative specificity, and stability in sediments, the distribution and abundance of sterols and steranes preserved in sedimentary records have been long used in paleoenvironmental reconstructions (e.g., Grantham and Wakefield, 1988; Meyers and Ishiwatari, 1993; Hinrichs et al., 1999; Menzel et al., 2003; Knoll et al., 2007; Kasprak et al., 2015; Brocks et al., 2017).

### 3.7.2 Applications

While sterols have been successfully applied in paleolimnological studies to trace changes in algal and other organic matter sources (e.g., Aristegui et al., 1996; Matsumoto et al., 2003; Tani et al., 2009) or redox changes (Matsumoto et al., 2003), few studies have explored the full potential of the ecological and environmental information encoded in their stable isotopic composition. The stable carbon isotope composition ( $\delta^{13}\text{C}$ ) of sterols, as well as other algal lipids, is controlled by multiple biological and environmental factors, including the isotopic composition of dissolved inorganic carbon (DIC), carbon transport mechanisms, isotopic fractionation during carbon fixation and biosynthesis, growth rates, cell geometry, and nutrient availability, among others (Pancost et al., 1999; Popp et al., 1999; Schouten et al., 1998, Hayes, 2001; Pancost and Pagani, 2006; Cernusak, et al., 2013). Thus, if some of the factors controlling their stable isotope composition can be constrained, the  $\delta^{13}\text{C}$  of sterols present in aquatic environments can be used to, for instance, disentangle changes in biological sources (e.g., algal vs. land plants; Matsumoto et al., 1982; Canuel et al., 1997; Neunlist et al., 2002; Chikaraishi et al., 2005; Chikaraishi and Naraoka, 2005), the diagenetic transformation of sterols to stanols (Neunlist et al., 2002), the possible sources of other algal lipids such as alkenones (D'Andrea and Huang, 2005), and prevailing biogeochemical conditions (e.g., nutrient availability, carbon cycling, primary productivity, the concentration and isotopic composition of inorganic carbon pools, changes in column stratification; Hollander and Smith, 2001; Villinski et al., 2008). A step forward in tracing the specific sources of organic matter preserved in lacustrine environments is the paired analysis of carbon and hydrogen stable isotopes in sterols ( $\delta^{13}\text{C}$ - $\delta^2\text{H}$ ). By using the  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  sterols present in Lake Haruna, Japan, Chikaraishi and Naraoka (2005) were able to disentangle the complexity of single and mixed (aquatic vs. terrestrial) sources in this setting. For instance, while the  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  values of sedimentary 24-methylcholesta-5,22-dien-3 $\beta$ -ol corresponded well to those of planktonic algae, the  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  of sterols such as 24-ethylcholest-5-en-3 $\beta$ -ol indicated a mixture of sources from terrestrial  $\text{C}_3$  plants and planktonic algae (Fig. 14). Overall, the results from this study confirmed observations that  $27\Delta^{5,22}$ ,  $27\Delta^5$ ,  $27\Delta^0$ , and  $28\Delta^{5,22}$  sterols are algal products, while  $28\Delta^5$ ,  $29\Delta^{5,22}$ , and  $29\Delta^5$  sterols can derive from multiple sources, thus allowing their more reliable use in paleolimnological and paleoclimatic reconstructions.

The  $\delta^{13}\text{C}$  of sterols, along with other algal and bacterial biomarkers preserved in lake sediments, has also been utilized to develop eutrophication models over time (Hollander and Smith, 2001). By studying the diversity, mass accumulation rate, and  $\delta^{13}\text{C}$  of biomarkers present in sediment from Lake Mendota (south-central Wisconsin, USA), in addition to the present-day isotopic dynamics in the lake water column, these authors produced eutrophication models (from moderate to severe) that take into account changes in eukaryotic-

and microbially-derived productivity over time. Notably, these models allow to explain how microbially-mediated carbon cycling processes can influence the  $\delta^{13}\text{C}$  record of bulk sedimentary organic carbon, and thus provide insight into interpreting carbon isotopic trends preserved in lacustrine records. Additionally, the presence of  $^{13}\text{C}$ -depleted sterols in sediment of Ace Lake in Antarctica was used to constrain the presence of aerobic methanotrophic bacteria and an active methane cycle in this setting during the Holocene (Coolen et al., 2004b).



**Figure 14:** Cross plots of  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  of  $28\Delta^5$ ,  $29\Delta^{5,22}$ , and  $29\Delta^5$  sterols from the Lake Haruna environment. Open and filled symbols indicate the naturally occurring i.e. “free” sterols and bound forms, respectively (modified from Chikaraishi and Naraoka, 2005).

More recently, along with other algal lipids such as alkenones (Section 3.2), the  $\delta^2\text{H}$  of sterols present in aquatic environments has increasingly been used as a proxy for the  $\delta^2\text{H}$  of environmental water ( $\delta^2\text{H}_{\text{water}}$ , see review by Sachse et al., 2012). Sauer et al. (2001b) first showed that the  $\delta^2\text{H}$  of 24-methylcholest-3-ol, 24-ethylcholest-5,22-dien-3-ol, and 4,23,24-trimethylcholesterol extracted from aquatic sediments exhibited a rather constant fractionation (around  $\sim 201 \pm 10\text{‰}$ ) with respect to environmental water. Since then, a growing body of research has demonstrated that, besides  $\delta^2\text{H}_{\text{water}}$ , biological factors such as biosynthetic pathways, secondary hydrogen exchange, growth rates, in addition to environmental factors

such as salinity, temperature, and nutrient availability can influence hydrogen isotope fractionation and the  $\delta^2\text{H}$  of sterols (Sessions et al. 1999, Li et al. 2009, Chikaraishi et al. 2004, Zhang and Sachs 2007; Zhang et al., 2009; Sachse et al., 2012; Romero-Viana, 2013; Nelson and Sachs, 2014). Over the past few years, the  $\delta^2\text{H}$  of source-specific sterols such as dinosterol have also been shown to be controlled by salinity. The  $\delta^2\text{H}$  of dinosterol present in suspended particles and surface sediment from the Chesapeake Bay (salinity range of 10–29 PSU) exhibits a  $^2\text{H}/^1\text{H}$  fractionation that decreases by  $0.99 \pm 0.23$  per unit increase in salinity (Schwab and Sachs, 2011). While the exact mechanism controlling isotopic fractionation under varying salinity remains elusive, the observed relationship in sterols and other lipids supports qualitative to semi-quantitative reconstructions of past salinities from sedimentary dinosterol  $\delta^2\text{H}$  values. For example, the  $\delta^2\text{H}$  of dinosterol preserved in sediments from a brackish lake in Palau (Sachs et al., 2009; Richey and Sachs, 2016) and an endorheic lake in Galápagos (Atwood and Sachs, 2014; Nelson and Sachs, 2016), have been used to infer variations in salinity and precipitation associated with latitudinal shifts in the position of the Intertropical Convergence Zone during the Late Holocene. The information embedded in the  $\delta^2\text{H}$  of sterols in sedimentary records, however, is gradually lost over geologic timescales due to hydrogen exchange with increasing thermal maturity (Sessions, 2016).

### **3.8 Sedimentary cellulose**

#### **3.8.1 Sources**

Cellulose is a structural carbohydrate and plays an essential role for cell growth and development of higher plants forming a major component of vascular plant organic matter (Khezami et al., 2005). Non-vascular plants, such as bryophytes and some algae (Rho and Litzky, 1979; Koyama et al., 1997), and bacteria (Ross et al., 1991) are also capable to synthesize cellulose. Potential sources for sedimentary cellulose are therefore terrestrial plants, soils, aquatic macrophytes, bacteria, and algae. Cellulose is biosynthesized from initial photosynthates (trioses) converted to hexoses and condensed to form cellulose (Hayes, 2001). Cellulose microfibrils, consisting of bundles of cellulose molecules, are completely embedded into a matrix of polysaccharides (hemicellulose) and small amounts of structural proteins in cell walls (Showalter, 1993; Popper et al., 2011) and, thus, not easily accessible for decomposing organisms.

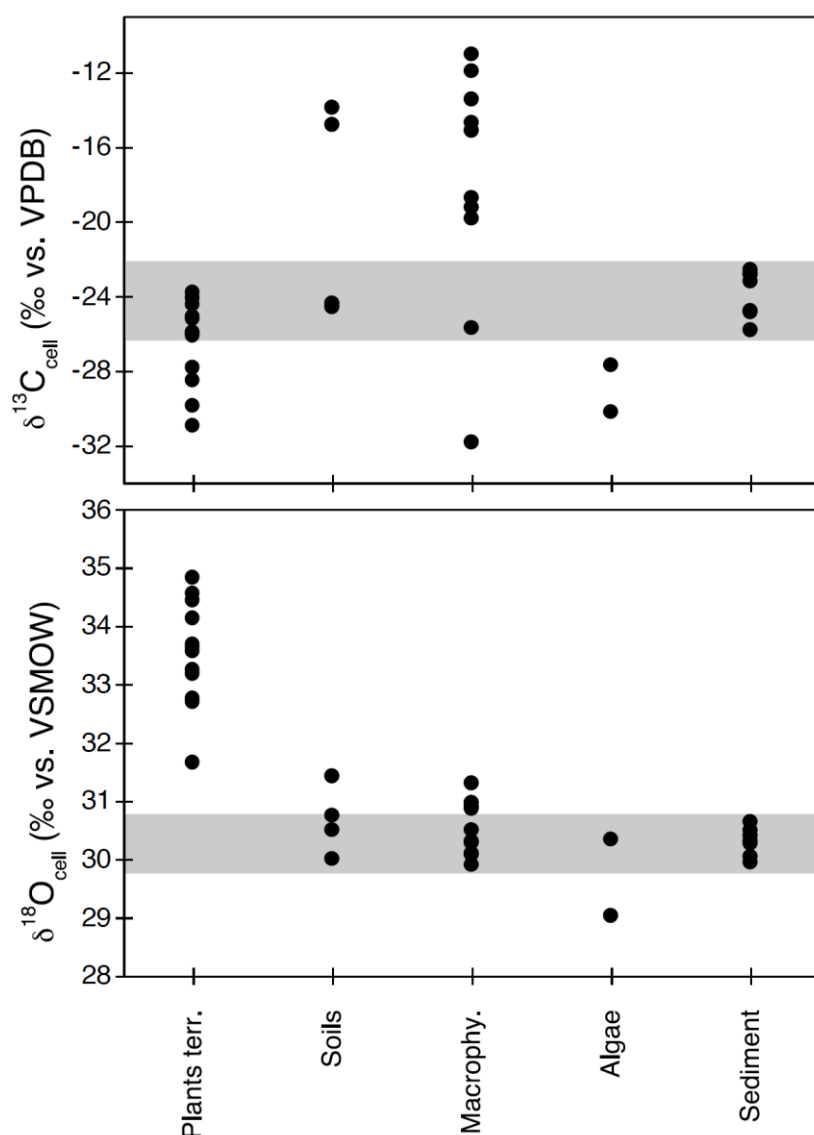
#### **3.8.2 Applications**

The isotopic composition of oxygen, carbon, and hydrogen in the molecular structure of aquatic cellulose provides information on cellulose origin, the lacustrine carbon cycle and the lake-water balance. Here, we focus on the determination of the oxygen isotope composition of sedimentary cellulose ( $\delta^{18}\text{O}_{\text{cell}}$ ), which either can be of terrestrial (litter, plant debris, soil) or

aquatic origin (aquatic macrophytes, algae, bryophytes). The  $\delta^{18}\text{O}$  value of aquatic cellulose is closely linked to the host water isotopic composition (Sauer et al., 2001a; Sternberg et al., 2007; Zhu et al., 2014a; Mayr et al., 2015), while terrestrial cellulose is generally more  $^{18}\text{O}$ -enriched due to soil evaporation and leaf water transpiration (Roden et al., 2000). In many cases, aquatic and terrestrial cellulose sources contribute to bulk sediment  $\delta^{18}\text{O}_{\text{cell}}$  values, which is a challenge for paleoenvironmental interpretation. In this respect, multiple-proxy approaches, including analyses of C/N ratios of bulk sediment and  $\delta^{13}\text{C}$  of cellulose, can give valuable clues for interpretation (Heyng et al., 2014, c.f. Figure 15). Alternatively, identifiable cellulose-containing macrofossils can be extracted from the sediment and analysed. Hence, some studies focus on cellulose extracted from aquatic moss remains in sedimentary sequences (Mayr et al., 2013; Zhu et al., 2014b). In other cases, the environmental setting precludes major terrestrial cellulose input, e.g. for lakes with very small or scarcely vegetated catchments (Heyng et al., 2014).

The  $\delta^{18}\text{O}$  values of cellulose, calcite and diatom opal from the Last Glacial to Holocene time intervals of the sediment record of Polish Lake Gosciaz were analysed to disentangle host water isotope variations from temperature changes (Rozanski et al., 2010). While at least two unknowns, temperature and host-water  $\delta^{18}\text{O}$ , influence calcite and opal  $\delta^{18}\text{O}$  values,  $\delta^{18}\text{O}_{\text{cell}}$  was used to directly reconstruct host-water  $\delta^{18}\text{O}$  and thus resolve temperature- $\delta^{18}\text{O}$  equations of the other proxies. A similar approach was used for a 6000-year long, Holocene record from Lake Pupuke, New Zealand (Heyng et al., 2015). In that study,  $\delta^{18}\text{O}$  values of biogenic opal and  $\delta^{18}\text{O}_{\text{cell}}$  were combined to reconstruct fluctuations of lake-water temperatures and compared with independent temperature reconstructions using GDGTs. Both temperature reconstructions matched comparatively well. In dry regions, the lake-water-isotope composition is strongly influenced by evaporative heavy-isotope enrichment. Host-water-isotope reconstructions from  $\delta^{18}\text{O}_{\text{cell}}$  can then provide information about past lake-water balance and regional hydrology in such areas. Zhu et al. (2014b) used  $\delta^{18}\text{O}_{\text{cell}}$  of submerged aquatic mosses from sediments of Laguna Potrok Aike to reconstruct lake-water  $\delta^{18}\text{O}$  of this Patagonian steppe lake during the last deglaciation.





**Figure 15:** Stable isotope composition of cellulose from autochthonous and allochthonous sources and sediment from a modern survey at Lake Pupuke (Heyng et al., 2014). Shown are  $\delta^{13}\text{C}_{\text{cell}}$  (upper) and  $\delta^{18}\text{O}_{\text{cell}}$  (lower) values from terrestrial plants, soils, aquatic macrophytes, lacustrine algae, and lake sediments (upper 30 cm). Grey bars indicate the range of Lake Pupuke's sediments. Note the  $^{13}\text{C}$  enrichment of aquatic macrophytes in that lake, while terrestrial plant cellulose is strongly  $^{18}\text{O}$  enriched compared to other sources and sediments.

### 3.9 Organic sulfur compounds

#### 3.9.1 Sulfur sources

The use of stable isotopes to understand the biogeochemical cycling of sulfur in oceanic (Rees et al., 1978; Jørgensen et al., 2004; Böttcher et al., 2006), freshwater (Fry, 1986; Canfield et al., 2010; Zerkle et al., 2010), and terrestrial systems (Goldhaber and Kaplan, 1980; Habicht and Canfield, 2001) has principally focussed on the dynamics of inorganic sulfate, sulfide and their intermediate species. Organic sulfur compounds (OSCs) in sedimentary organic matter

are predominantly incorporated via secondary processes (Werne et al., 2008). The major sulfurization pathway involves an abiotic reaction of reduced inorganic sulphur species during diagenesis (e.g., pore water  $\text{HS}^-$ ; or polysulfides,  $\text{S}_x^{2-}$ ) that is produced by microbial sulfate reduction (Kaplan and Rittenberg, 1964; Fry et al., 1986). OSCs deposited from biological sources (e.g., the amino acid cysteine), which are synthesized through direct reduction and assimilation of dissolved sulfate, are very labile to diagenetic loss (Hedges, 1992; Hedges and Keil, 1995), but may still contribute to sedimentary organic matter which commonly has  $\delta^{34}\text{S}$  values that range between those of biotic (relatively high  $\delta^{34}\text{S}$ ) and abiotic (lower  $\delta^{34}\text{S}$ ) end members (Canfield et al., 1998; Passier et al., 1999; Werne et al., 2003; Aizenshtat and Amrani, 2004). Few studies (e.g., Amrani et al., 2009; Oduro et al., 2011, 2012) have looked at the S isotope composition of OSC.

Thermochemical sulfate reduction (TSR) can also contribute high concentrations of OSCs in gas (i.e., high  $\text{H}_2\text{S}$ ) reservoirs. TSR is a high temperature redox process in which sulfates, such as gypsum or anhydrite, are reduced and organic matter oxidised (Krouse et al., 1988; Cross et al., 2004). TSR can significantly influence the  $\delta^{34}\text{S}$  of OSCs, which will gradually inherit the  $\delta^{34}\text{S}$  value of the mineral sulfates utilised, these are typically relatively heavy compared to OSCs from reduced S sources (Amrani et al., 2012).

In recent years the advent and utilization of quadruple sulfur isotopes ( $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$ ) has allowed for increased resolution and fingerprinting of the biological and abiotic processes that govern sulfur cycling. The minor isotopes ( $^{33}\text{S}$ , and  $^{36}\text{S}$ ) are subject to inorganic and organic fractionation mechanisms that are similar to those for  $^{34}\text{S}$ . Experimental studies have shown that biological S metabolisms produce minor isotope patterns, with characteristics attributed to differences in the individual step controls of the metabolic pathways (Farquhar et al., 2003, 2007; Johnston et al., 2005, 2007, 2008; Ono et al., 2006). The incorporation of minor isotopes into studies allows for fuller characterisation within biogeochemical systems (at both the cellular and ecosystem level) and as such can be used to assess the contribution of different pathways (enzymatic or biogeochemical) to the measured isotopic values.

### **3.9.2 Applications**

Early biogeochemical applications of CSIA of sulfur-containing compounds have included studies of the mechanism and timeframes of diagenetic organic sulfurization and cycling in sediments, the characterisation of ocean-derived sulfur aerosols, exploration for oil and mineral resources and other paleo-environmental reconstructions. Further details of the first of these, as applied to modern settings, follow:

#### *Diagenetic sulfurization pathways*

A combination of syngeneic (water column) and diagenetic (sediment) S sources in immature sediments from the Cariaco Basin were identified by  $\delta^{34}\text{S}_{\text{OSCs}}$  (Raven et al., 2015). These two main organic sulfurization mechanisms consisted of:

i) Reaction of dissolved  $\text{HS}^-$  with OM resulting in the intra-molecular addition of available S. Difficulties in releasing intra-molecularly bound S make this a relatively irreversible reaction. The incorporation of  $^{32}\text{S}$  would be kinetically favored, thus, leading to organic S lower in  $^{34}\text{S}$  than  $\text{HS}^-$  and more similar to co-existing pyrite.

ii) Reaction of OM with polysulfides ( $\text{S}_x^{2-}$ ) resulting in an intermolecular addition and formation of  $\text{S}_x$ -bridges between different organic units. A reverse of this process could subsequently release the  $\text{S}_x$ -bridges from the organic moiety, such that  $\delta^{34}\text{S}$  of this organic S would be reflective of the equilibrium status of these reactions.

Raven et al. (2015) considered pathway ii) to be most likely responsible for the relative  $^{34}\text{S}$  enrichment (e.g. Amrani and Aizenshtat, 2004) traditionally attributed to organic sulfurization and the formation of the kerogen fraction.

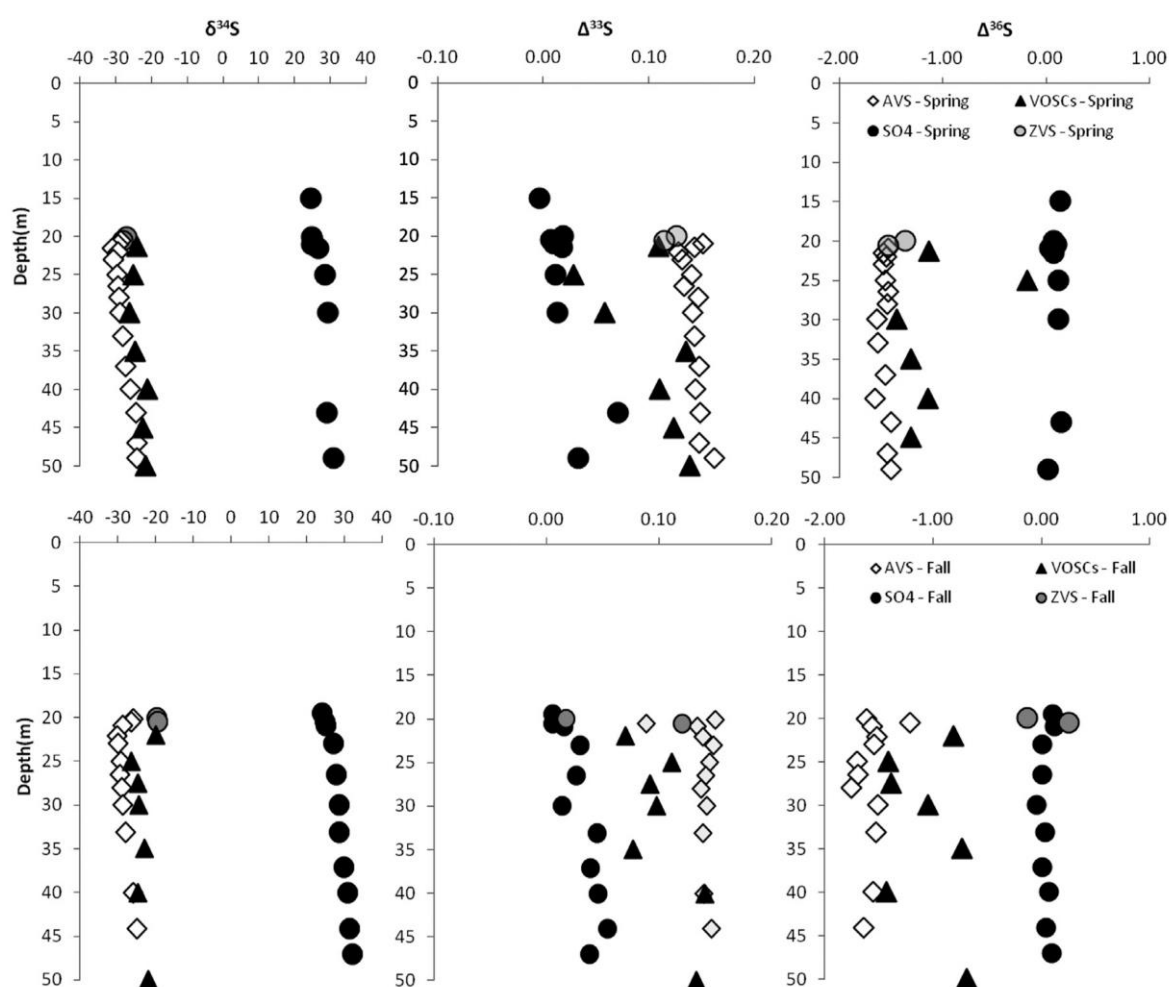
#### *Tracing organic sulfur cycling in modern lakes*

Oduro et al. (2013) and Zerkle et al. (2010) utilized quadruple S isotope systematics and zero-valent sulfur (ZVS), volatile organic sulfur compounds (VOSCs) and acid-volatile sulfur (AVS) profiles as part of a multi-year study on the meromictic Fayetteville Green Lake (FGL, Fig. 16). Stratification in the lake is mainly controlled via the inflow of highly saline groundwater, resulting in a strongly developed chemocline, while the source of both organic and inorganic sulfur is from high sulfate concentration in the water column. These conditions make the site a natural analogue for ancient environments.

Zerkle et al. (2010) showed that at the chemocline sulfide is enriched in  $^{34}\text{S}$  as a result of sulfide oxidation via reaction with  $\text{O}_2$ , from the oxidized freshwater above, in spite of the high population of phototrophic S-oxidizing organisms observed at the chemocline. They further suggested that the production of product sulfur species, e.g., thiosulfate, sulfite, or zero-valent sulfur, was a result of very fast turnover of S-intermediates by oxidation and/or disproportionation processes around the chemocline. Their data also showed seasonal variations in isotopic enrichment at the chemocline as a result of greater contribution from phototrophic S-oxidation reactions under higher light availability in spring and summer. ZVS in the chemocline in autumn is suggested to reflect production and re-oxidation by phototrophic processes, including intercellular isotope exchange between  $\text{S}_0$ , polysulfides, and sulfide, and further oxidation of ZVS to sulfate. Smaller fractionations between sulfide and

zero-valent sulfur in April suggest a metabolic rate control on the extent of fractionation, similar to that of sulfate-reducing prokaryotes.

Oduro et al. (2013) built upon this study by quantifying VOSCs in the lake and highlighting the various biotic and abiotic pathways available for methylated and non-methylated VOSCs production and cycling in sulfidic freshwater environments (Fig. 16). These applications, while focused on modern-day lakes, have implications for our abilities to identify such processes in the preserved horizons of paleolakes and similar environments. While such studies of VOSCs in the ancient rock record are limited due to issues of maturity, the overprints and alteration, greater understanding of these processes in modern analogues may provide a new way to fingerprint products of these processes that are identifiable in the rock record. Further, with the development of new analytical techniques, greater machine resolution, the ability to screen, and reduce, post-deposition organic contaminants, and better sample processing (e.g., Brocks et al., 2008; Brocks and Hope, 2013) we can hope to soon be able to readily identify these compounds in the rock record.



**Figure 16:** Depth profiles of the multiple sulfur isotope composition of different sulfur species (Sulfate –  $\text{SO}_4^{2-}$ , Acid Volatile Sulfur - AVS, Volatile Organic Sulfur Compounds – VOSCs, and

Zero-Valent Sulfur – (ZVS) in Fayetteville Green Lake (FGL) for Spring, 2009 and Fall, 2008. From Oduro et al., 2013, including data from Zerkle et al., 2010)

In addition, the studies discussed above highlighted the role of simultaneous biological and abiotic processes in freshwater environments that promote the formation of VOSCs and then their diffusion to the atmosphere. Further characterization of these processes will aid in improving estimate of the atmospheric sulfur budget in present and Recent times.

## **4 SUMMARY AND OUTLOOK**

Over the past four decades, applications of CSIA have vastly expanded into multiple paleoenvironmental applications using an extended range of isotopes and ever more sophisticated analytical techniques. The study of carbon and hydrogen isotopes of hydrocarbons such as *n*-alkanes is by now well-established as they are non-functionalized, of well-understood origin and straightforward to analyse. However, there remain a number of challenges, and particularly so for compounds where the biosynthetic pathway is not fully understood, the source varies, or where there are analytical constraints.

### **4.1 General problems**

#### ***i) Biosynthesis***

It has been observed that compounds produced through different biosynthetic pathways can differ in their carbon isotope value by up to 20% within an individual organism (e.g., Summons et al., 1994; Schouten et al., 1998; van der Meer et al., 1998). However, the exact mechanisms leading to these isotopic differences are often not well-constrained (Hayes, 2001), which may lead to ambiguous results unless biochemical studies improve our understanding of differentiated fractionation within source organisms of biomarkers targeted by CSIA.

#### ***ii) Ecological factors***

A key factor imposing carbon and hydrogen isotopic variation in land plants is water-use efficiency, as observed in C3, C4 and CAM plants (Ehleringer et al., 1993), which is controlled by local hydrology. In case of aquatic organisms, a range of ecological factors has been found to inflict isotopic variation, including the partial pressure of CO<sub>2[aq]</sub> (*p*CO<sub>2[aq]</sub>), cell size and geometry (Goericke et al., 1994; Popp et al., 1998), virus interactions and the growth rate of phytoplanktonic cells (Laws et al., 1995; Bidigare et al., 1997; Chivall et al., 2014). These findings highlight the need of culture studies, in particular, of lacustrine primary producers since most of such investigations so far, like the ones cited above, have been aimed at marine or coastal species.

#### ***iii) Source uncertainties***

*In-situ* microbial biomass may add to and bias CSI data of supposedly aquatic or terrestrial sources, and the distinction between genuine change in the isotopic composition of sedimentary compounds and changing proportions of *in-situ* biomass often poses a challenge. In this context, combining biomarker CSI and rDNA analyses in order to pin down the source of specific microbial compounds appears highly promising (e.g., Coolen et al., 2004b).

We have already pointed out some of the more specific challenges associated to isotope analyses of the various compound classes discussed in Section 3. However, challenges typically come along with opportunities, in this case, of further paleolimnological information gained through extended approaches to CSIA, which we expand on in the following.

#### **4.2 Targeting the C and H of alkyl lipids – the easy, the tricky, and the prospective**

Applications of CSIA of alkyl lipids as presented in Section 3.1 illustrate the great potential of such measurements for the development of paleohydrological proxies in Quaternary paleolimnology on a range of different time-scales, from the early Pleistocene to the Holocene. However, these examples, as well as recent reviews (e.g., Eglinton and Eglinton, 2008; Sachse et al., 2012; Reiffarth et al., 2016; Sessions, 2016; Diefendorf and Freimuth, 2017), also indicate some gaps in our understanding of alkyl lipid stable isotopes. The fractionation pathways of stable carbon isotopes and stable hydrogen isotopes, in particular, need to be better understood in order to be able to arrive at robust reconstructions of paleohydrological changes. Changes in species distribution in response to ecosystem adaption to environmental change alone may be responsible for significant change in the  $\delta^2\text{H}$  values of non-species-specific aquatic biomarkers (e.g., Rach et al., 2017). Laboratory-based growth experiments as well as studies of isotope fractionation in modern ecosystems continue to expand the knowledge of the biogeochemical fingerprint of the various OM sources and our understanding of the origins and functions of alkyl lipids through time. Despite the many influences on the  $\delta^2\text{H}$  or  $\delta^{13}\text{C}$  values of alkyl lipids in environmental archives, much of the variability that results, e.g., from seasonality or the patchiness of organic matter sources in the catchment of the studied archive is averaged out due to intermediate storage of the compounds over extended time intervals in soils and/or along transport across the catchment (e.g., Oakes and Hren, 2016). Still, the effects of changes in the source vegetation on CSI records are often understudied and cannot be determined by isotope analysis alone (e.g., Hadley et al., 2008; Rach et al., 2017). Studies combining independent indicators of vegetation change, such as pollen or macrofossil analysis, and compound-specific stable isotope analyses can highlight where factors other than climate played a role. Such information is especially needed when, e.g.,  $\delta^2\text{H}$ -records of long-chain *n*-alkyl lipids are used to calculate terrestrial evaporation (e.g., Sachse et al., 2004; Rach et al., 2014) as this has been problematic in cases where vegetation was diverse and showed spatiotemporal variability (e.g., Berke et al., 2012; Rao et al., 2014;

Rach et al., 2017; van den Bos et al., 2018).

Furthermore, the importance of the soil organic matter pool as a source of biomarkers in sedimentary records is increasingly recognised. Systematically changing offsets, for example, in  $\delta^{13}\text{C}$  values between suberin-derived mid-chain ( $\text{C}_{22}$ ) and cuticular long-chain lipids ( $>\text{C}_{26}$ ) have been reported (Holtvoeth et al., 2017). However, despite the apparent environmental control, they cannot be interpreted unless the mechanisms behind the mismatch between cuticular and suberin alkyl lipid CSI are understood. In this context, the transport pathways of biomarkers from their source to the sediment archive are currently understudied. Specific organic matter fractions are likely associated to certain grain size fraction in soils as well as sediments (Baldock and Skjemstad, 2000; Gentsch et al. 2015; Wakeham and Canuel, 2016). Therefore, the combination of paleohydrological and mineralogical data with source-sensitive CSI data is advisable. Where possible, alkyl lipids and their isotope values from extant sources should be investigated in order to reduce the uncertainty in the interpretation of CSI data from environmental archives (e.g., Eley et al., 2016). Studies that use multiple *n*-alkyl compounds (e.g., *n*-alkanes, *n*-alkanoic acids) or combine  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  measurements are still few but will likely enhance our understanding of how alkyl lipids are ultimately preserved in geological records (Sachse et al., 2012; Sessions, 2016; Diefendorf and Freimuth, 2017).

Long-chain alkenones remain a challenge for CSI studies in lakes due to the biodiversity of their source organisms and, therefore, the uncertainty associated to the ecological drivers of lacustrine alkenone production and isotope fractionation during biosynthesis. Similar to the marine biome, salinity appears to be a major factor affecting the  $\delta^2\text{H}$  value of lacustrine alkenones, in addition to assumed effects of growth rate (e.g., Chivall et al., 2014). Thus,  $\delta^2\text{H}$  values of lacustrine alkenones may potentially be applied to lake systems that experienced large climatically controlled changes in salinity throughout their evolution once the sources of the alkenones have been ascertained. As phylogenetic shifts among the alkenone producers are also likely to correlate with environmental changes, it appears advisable to combine CSI with DNA studies of alkenone producers in both modern and ancient contexts, in particular, with regard to alkenone producers in freshwater systems that are currently under-investigated.

#### **4.3 Propping up steroids and hopanoids**

The  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  of algal sterols and steranes offers great potential for the reconstruction of Quaternary ecosystems and environments. This includes changes in organic matter sources, shifts in algal communities and productivity, as well as variations in the isotopic composition of DIC and meteoric water, and salinity. However, the need for multiple purification steps prior to analysis and for correction of the determined isotope ratio for derivatised carbon and hydrogen atoms currently precludes a more routine use of sterols in high-resolution

paleoenvironmental studies. Dinosterol has become the most commonly used sterol for CSI analysis, particularly for  $\delta^2\text{H}$ , due to its biological specificity compared to other sterols. Several new preparatory protocols using high performance liquid chromatography (HPLC) have been developed for its purification from complex sterol/alcohol mixtures (e.g., Smittenberg and Sachs, 2007; Atwood and Sachs, 2012; Nelson and Sachs, 2013).

CSIA determined from hopanes will have continued utility in deconvolving modern and ancient carbon cycling. Whereas bacterial inputs, especially with respect to inputs of methanotroph-derived material (c.f. Talbot et al 2014; Raghoebarsing et al., 2005), as such do not demonstrate that methanotrophy was actually taking place, significantly  $^{13}\text{C}$ -depleted hopanoids are difficult to explain otherwise. Stable isotope probing and “pulse-chase” experiments are likely to offer substantial advances in understanding the applications and limitations of compound-specific isotope analysis of hopanoids (Crossman et al., 2001). CSIA of derivatized BHPs improves our ability to analyze compounds with potentially greater source/metabolic specificity; this will certainly fuel new and broader applications. For instance, further work on applications of the BHT isomer as a potential biomarker for anammox activity will greatly expand our knowledge of the complexity of nitrogen fixation processes in lacustrine ecosystems. A better understanding of the drivers of hopanoid synthesis will improve application of all hopanoid-based proxies. Coupling hopanoid CSIA with archaeal lipids is a powerful approach to reconstructing prokaryotic roles in past ecosystems and response to environmental change.

#### **4.4 Shedding light on pigments**

Research into disentangling the complex array of factors that affect the synthesis, transformation and sedimentation of pigment transformation products in the modern environment is required to facilitate a more rigorous approach to interpreting isotope ratios in pigments extracted from sediments. For example, we can anticipate that further work on phaeopigments, such as limnic phaeophytin and pyropheophytin (Tyler et al., 2010), especially in redox-stratified basins (Fulton et al., 2018), will improve paleoenvironmental interpretations of chlorin-specific isotopic data. In addition, studies focused on environmental conditions, including the impact of oxygen (particularly in the case of maleimides, c.f. Naeher et al. 2013) can assist the development of novel proxies for estimating the degree of organic matter degradation on a variety of timescales.

#### **4.5 Buttressing cellulose**

Interpretation of sedimentary cellulose  $\delta^{18}\text{O}$  values for reconstructions of lake-water  $^{18}\text{O}$  (Section 3.6.2) has to consider that variable contributions of terrestrial cellulose can modify the aquatic isotope signal. The choice of adequate sites with scarcely vegetated catchment is



one option to overcome this potential bias. Methodological difficulties may have also biased previous results (Beuning et al. 2002). The development of the CUAM method for cellulose extraction (Wissel et al., 2008) therefore was a milestone for gaining pure cellulose from sediments albeit its potential is not yet fully explored due to the scarcity of comparative studies. The applicability of the method is sometimes limited by low content of cellulose in lacustrine sediments, which is typically in the order of 0.1 wt% in productive lakes (Heyng et al., 2014). Uncertainties still exist regarding the exact oxygen-isotope fractionation factors between source water and cellulose, possibly due to methodological challenges. Reported fractionation values vary between 25 ‰ and 32 ‰ according to different studies and preparation methods (Wolfe, et al. 2001; Mayr et al. 2013, 2015). The occurrence of a temperature effect on oxygen-isotope fractionation during cellulose formation is still discussed (Sternberg and Ellsworth, 2011; Mayr et al., 2013). A potential methodological extension is the recent development of an analytical procedure for  $\delta^{18}\text{O}$  analyses on hemicellulose-derived sugar biomarkers (Zech et al., 2014; Hepp et al., 2015).

#### **4.6 Sulfur on the horizon**

Compound-specific  $\delta^{34}\text{S}$  analysis will help to illuminate the operation of organic sulfur cycles of the past and present. A rapid transition is anticipated from the current practice of measuring the bulk  $\delta^{34}\text{S}$  isotopic value of whole sediments or major organic fractions to measuring the  $\delta^{34}\text{S}$  composition of individual molecular species – similar to the uptake of compound specific  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  technologies. Further maturity of the technology for CSIA of sulfur-containing compounds should lead to greater improvements in analytical performance (i.e., precision and reproducibility  $<\pm 0.5$  ‰) and further targeted application leading to a better understanding of the properties, interactions and fate of organic sulfur in lake basins.

#### **4.7 Stones unturned**

Although the understanding of the various fractionation factors associated to amino acid biosynthesis and metabolism is constantly improving, the fact that they also have a low preservation potential in lacustrine sediments may limit their applicability for paleoenvironmental studies. Still, as demonstrated by Carstens et al. (2013) for shallow sediments (6 cm) of an oligotrophic and a eutrophic lake,  $\delta^{15}\text{N}$  values of amino acids did preserve the different trophic status of the two lakes. Thus, for studies that aim to investigate recent anthropogenic ecosystem change, e.g., in the context of industrialization or urbanization, amino acid  $\delta^{15}\text{N}$  values may hold promising information on changes in nutrient loading, while the limit of such an approach going back in time remains to be tested.

Some compounds have been frequently observed but appear notoriously understudied. One such example is loliolide and its epimer, iso-loliolide. They represent the end pieces of the

carotenoid pigment fucoxanthine (Fig. 10) and are formed in equal quantities during the anaerobic degradation of the compound (Repeta, 1989), which is the main pigment in diatoms but also occurs in dinoflagellates and haptophytes (Repeta and Gagosian, 1982; Klok et al., 1984). Loliolide and iso-loliolide are frequently detected in marine sediments (Repeta and Gagosian, 1982; ten Haven et al., 1987; Repeta, 1989; Hinrichs et al., 1999b; Menzel et al., 2003) but have also been found in significant amounts in sediments of Lake Kivu (Al-Mutlaq et al., 2008), Lake Malawi (Castañeda et al., 2009, 2011), Lake Challa (van Bree et al., 2018) and Lake Ohrid (J. Holtvoeth, unpublished data). While they have been used as biomarkers for diatoms for reconstructing changes in the marine (Hinrichs et al., 1999b) and limnic phytoplankton community (Castañeda et al., 2009, 2011; van Bree et al., 2018), only Menzel et al. (2003) determined the  $\delta^{13}\text{C}$  values of loliolide/iso-loliolide in eastern Mediterranean sediments in order to find evidence for productivity changes during sapropel deposition. We are not aware of any CSI study of these biomarkers in a lacustrine context where, e.g., changes in salinity,  $\text{CO}_2$  limitation or productivity could potentially be targeted through CSIA of these algal compounds. The  $\delta^{13}\text{C}$  of the planktonic iGDGTs has also been reported to contain some information about  $p\text{CO}_2$  in marine environments (Kuypers et al., 2002; Pearson et al., 2016). As iGDGTs are also common in lake environments (Powers et al., 2004), they could be exploited for this purpose.

Finally, there is much scope for extending CSIA in future analytical technologies. These include further applications of the relatively new analytical capability of compound-specific  $\delta^{34}\text{S}$  (Amrani et al., 2012), high-temperature GC-IRMS analysis of GDGTs (Lengger et al., 2018), and the possible expansion of a variety of preparatory LC-MS techniques for purification of steranes and hopanes. Also, the revolutionary ability to measure stable carbon and hydrogen isotopes at specific molecular positions (Eiler et al., 2017) radically enhances the details of the complex processes involved in the biosynthesis of molecules and usefulness as unique environmental informants.

## ACKNOWLEDGEMENTS

JHW is supported by an Annual Adventures in Research Award from University of Southampton and NSF EAR 1349650, FSF is supported by a PhD scholarship (grant number BEx 9541-13/6) from the Science without Borders Programme (Ciência sem Fronteiras), sponsored by the CAPES Foundation within Ministry of Education, Brazil. SCJ is supported by iCrag under the Science Foundation Ireland, EU Regional Development Fund and industry partners, as well as SFI research grant number 16/RP/3849. SKL was supported by Rubicon fellowship 825.14.014 from the Netherlands Organisation for Scientific Research NWO.

## REFERENCES

- Abella, C., Montesinos, E., Guerrero, R., 1980. Field studies on the competition between purple and green sulfur bacteria for available light (Lake Siso, Spain). In: Dokulil, M., Metz, D., Jewson, D. (eds.), *Developments in Hydrobiology*, 3. Junk, The Hague, pp. 173–181.
- Aichner, B., Herzsuh, U., Wilkes, H., Vieth, A., Böhner, J., 2010a.  $\delta D$  values of *n*-alkanes in Tibetan lake sediments and aquatic macrophytes - A surface sediment study and application to a 16ka record from Lake Koucha. *Org. Geochem.* 41, 779-790. doi: 10.1016/j.orggeochem.2010.05.010
- Aichner, B., Wilkes, H., Herzsuh, U., Mischke, S., Zhang, C., 2010b. Biomarker and compound-specific  $\delta^{13}C$  evidence for changing environmental conditions and carbon limitation at Lake Koucha, eastern Tibetan Plateau. *J. Paleolimnol.* 43, 873–899. DOI 10.1007/s10933-009-9375-y
- Aizenshtat Z. and Amrani, A., 2004. Significance of  $\delta^{34}S$  and evaluation of its imprint on sedimentary organic matter I. The role of reduced sulfur species in the diagenetic stage: a conceptual review. *Geochem. Soc. Spec. Pub.* 9, 15-33. doi:10.1016/S1873-9881(04)80004-X
- Alewell, C., Birkholz, A., Meusbürger, K., Schindler Wildhaber, Y., Mabit, L., 2016. Quantitative sediment source attribution with compound-specific isotope analysis in a C3 plant-dominated catchment (central Switzerland). *Biogeosci.* 13, 1587-1596. doi:10.5194/bg-13-1587-2016
- Amrani, A. and Aizenshtat, Z., 2004. Mechanisms of sulfur introduction chemically controlled:  $\delta^{34}S$  imprint. *Org. Geochem.* 35, 1319-1336. doi:10.1016/j.orggeochem.2004.06.019
- Amrani, A., Sessions, A.L., Adkins, J.F., 2009. Compound-specific  $\delta^{34}S$  analysis of volatile organics by coupled GC/multicollector-ICPMS. *Anal. Chem.* 81, 9027-9034. doi:10.1021/ac9016538
- Amrani, A., Sessions, A.L., Tang, Y., Adkins, J.F., Hills, R.J., Moldowan, M.J., Wei, Z., 2012. The sulfur-isotopic compositions of benzothiophenes and dibenzothiophenes as a proxy for thermochemical sulfate reduction. *Geochim. Cosmochim. Acta* 84, 152-164. doi:10.1016/j.gca.2012.01.023
- Andreae, M.O., 1990. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. *Mar. Chem.* 30, 1-29. doi:10.1016/0304-4203(90)90059-L
- Atwood, A.R. and Sachs, J.P., 2012. Purification of dinosterol from complex mixtures of sedimentary lipids for hydrogen isotope analysis. *Org. Geochem.* 48, 37-46. doi:10.1016/j.orggeochem.2012.04.006

- 1714 Atwood, A.R. and Sachs, J.P., 2014. Separating ITCZ- and ENSO-related rainfall changes in  
1715 the Galápagos over the last 3 kyr using D/H ratios of multiple lipid biomarkers. *Earth Planet.*  
1716 *Sci. Lett.* 404, 408-419. doi:10.1016/j.epsl.2014.07.038
- 1717 Aristegui, J., Montero, M.F., Ballesteros, S., Basterretxea, G., van Lenning, K., 1996.  
1718 Planktonic primary production and microbial respiration measured by C-14 assimilation and  
1719 dissolved oxygen changes in coastal waters of the Antarctic Peninsula during austral  
1720 summer: implications for carbon flux studies. *Mar. Ecol. Progr. Series* 132, 191-201.  
1721 doi:10.3354/meps132191
- 1722 Baldock, J.A. and Skjemstad, J.O., 2000. Role of the soil matrix and minerals in protecting  
1723 natural organic materials against biological attack. *Org. Geochem.* 31, 697-710.  
1724 doi:10.1016/S0146-6380(00)00049-8
- 1725 Barber, C.N., Grice, K., Bastow, T.P., Alexander, R. Kagi, R.I., 2001. The identification of  
1726 crocetane in Australian crude oils. *Org. Geochem.* 32, 943-947. doi:10.1016/S0146-  
1727 6380(01)00057-2
- 1728 Berg, J.M., Tymoczko, J.L., Gatto, G.J., Stryer, L., 2015. *Biochemistry* - 8<sup>th</sup> edition, W.H.  
1729 Freeman, New York, pp.1120.
- 1730 Berke, M.A., Johnson, T.C., Werne, J.P., Grice, K., Schouten, S., Sinninghe Damsté, J.S.,  
1731 2012. Molecular records of climate variability and vegetation response since the Late  
1732 Pleistocene in the Lake Victoria basin, East Africa. *Quat. Sci. Rev* 55, 59-74. doi:  
1733 10.1016/j.quascirev.2012.08.014
- 1734 Beuning, K.R.M., Kelts, K., Russell, J., Wolfe, B.B., 2002. Reassessment of Lake Victoria–  
1735 Upper Nile River paleohydrology from oxygen isotope records of lake-sediment cellulose.  
1736 *Geology* 30, 559-562. doi:10.1130/0091-7613(2002)030<0559:ROLVUN>2.0.CO;2
- 1737 Bidigare, R.R., Fluegge, A., Freeman, K.H., Hanson, K.L., Hayes, J.M., Hollander, D., Jasper,  
1738 J.P., King, L.L., Laws, E.A., Milder, J., Millero, F.J., Pancost, R., Popp, B.N., Steinberg, P.A.,  
1739 Wakeham, S.G., 1997. Consistent fractionation of <sup>13</sup>C in nature and in the laboratory:  
1740 Growth-rate effects in some haptophyte algae. *Glob. Biogeochem. Cycles* 11, 279-292.  
1741 doi:10.1029/96GB03939
- 1742 Blaga, C.I., Reichart, G.-J., Schouten, S., Lotter, A.F., Werne, J.P., Kosten, S., Mazzeo, N.,  
1743 Lacerot, G., Sinninghe Damsté, J.S., 2010. Branched glycerol dialkyl glycerol tetraethers in  
1744 lake sediments: Can they be used as temperature and pH proxies? *Org. Geochem.* 41, 1225-  
1745 1234. doi:10.1016/j.orggeochem.2010.07.002
- 1746 Bloch, K., 1991. Cholesterol: evolution of structure and function. *New Compr. Biochem.* 20,

1747 363-381. doi:10.1016/S0167-7306(08)60340-3

1748 Blumenberg, M., Hoppert, M., Krüger, M., Dreier, A., Thiel, V., 2012. Novel findings on  
 1749 hopanoid occurrences among sulfate reducing bacteria: Is there a direct link to nitrogen  
 1750 fixation? *Org. Geochem.* 49, 1-5. doi:10.1016/j.orggeochem.2012.05.003

1751 Boreham, C.J., Summons, R.E., Roksandic, Z., Dowling, L.M., Hutton, A.C., 1994. Chemical,  
 1752 molecular and isotopic differentiation of organic facies in the Tertiary lacustrine Duaringa oil  
 1753 shale deposit, Queensland, Australia. *Org. Geochem.* 21, 685-712. doi:10.1016/0146-  
 1754 6380(94)90013-2

1755 Boschker, H.T.S., Moerdijk-Poortvliet, T.C.W., van Breugel, P., Houtekamer, M., Middelburg,  
 1756 J.J., 2008. A versatile method for stable carbon isotope analysis of carbohydrates by high-  
 1757 performance liquid chromatography/isotope ratio mass spectrometry. *Rapid Commun. Mass*  
 1758 *Spectrom.* 22, 3902-3908. doi:10.1002/rcm.3804

1759 Böttcher, M.E., Ferdelman, T.G., Jørgensen, B.B., Blake, R.E., Surkov, A.V., Claypool, G.E.,  
 1760 2006. Sulfur isotope fractionation by the deep biosphere within sediments of the eastern  
 1761 equatorial Pacific and Peru margin. In: Jørgensen, B.B., D'Hondt, S.L., Miller, D.J. (eds.),  
 1762 *Proc. ODP, Sci. Res.* 201, pp. 1-21.

1763 Bouchard, F., Turner, K.W., MacDonald, L.A., Deakin, C., White, H., Farquharson, N.,  
 1764 Medeiros, A.S., Wolfe, B.B., Hall, R.I., Pienitz, R., Edwards, T.W.D., 2013. Vulnerability of  
 1765 shallow subarctic lakes to evaporate and desiccate when snowmelt runoff is low. *Geophys.*  
 1766 *Res. Lett.* 40, 6112-6117. doi:10.1002/2013GL058635

1767 Bradley, A.S., Pearson, A., Sáenz, J.P., Marx C.J., 2010. Adenosylhopane: The first  
 1768 intermediate in hopanoid side chain biosynthesis. *Org Geochem* 41: 1075-1081.  
 1769 doi:10.1016/j.orggeochem.2010.07.003

1770 Brocks, J.J. and Summons, R.E., 2005. Sedimentary hydrocarbons - Biomarkers for early life.  
 1771 In: Schlesinger, W.H. (ed.), *Treatise on Biogeochemistry* 8, Elsevier, Amsterdam, pp. 63-  
 1772 115.

1773 Brocks, J.J. and Hope, J.M., 2013. Tailing of chromatographic peaks in GC-MS caused by  
 1774 interaction of halogenated solvents with the ion source. *J. Chrom. Sci.* 52, 471-475.  
 1775 doi:10.1093/chromsci/bmt068.

1776 Brocks, J.J., Grosjean, E., Logan, G.A., 2008. Assessing biomarker syngeneity using  
 1777 branched alkanes with quaternary carbon (BAQCs) and other plastic contaminants.  
 1778 *Geochim. Cosmochim. Acta*, 72, 871-888. doi:10.1016/j.gca.2007.11.028

- 1779 Brocks, J.J., Jarrett, A.J., Sirantoine, E., Hallmann, C., Hoshino, Y., Liyanage, T., 2017. The  
1780 rise of algae in Cryogenian oceans and the emergence of animals. *Nature*. 548, 578-581.  
1781 doi:10.1038/nature23457
- 1782 Brown, S.B., Smith, K.M., Bisset, G.M.F., Troxler, R.F. 1980. Mechanism of photo-oxidation  
1783 of bacteriochlorophyll *c* derivatives – a possible model for natural chlorophyll breakdown. *J.*  
1784 *Biol. Chem.* 255, 8063-8068.
- 1785 Bush, R.T. and McNerney, F.A., 2013. Leaf wax *n*-alkane distributions in and across modern  
1786 plants: Implications for paleoecology and chemotaxonomy. *Geochim. Cosmochim. Acta* 117,  
1787 161-179. doi:10.1016/j.gca.2013.04.016
- 1788 Callot, H.J., Ocampo, R., Albrecht, P., 1990. Sedimentary porphyrins: correlations with  
1789 biological precursors. *Energ. Fuels* 4, 635-639. doi: 10.1021/ef00024a002
- 1790 Callot, H.J. and Ocampo, R., 2000. Geochemistry of porphyrins. In: Kadish, K.M., Smith, K.M.,  
1791 Guilard, R. (eds.), *The Porphyrin Handbook: Volume 1*. Acad. Press, Burlington., pp.  
1792 349-398.
- 1793 Calvin, M. and Benson, A.A., 1948. The path of carbon in photosynthesis. *Science* 107, 476-  
1794 480. doi:10.1126/science.107.2784.476
- 1795 Canfield, D.E. and Thamdrup, B., 1994. The production of <sup>34</sup>S-depleted sulfide during bacterial  
1796 disproportionation of elemental sulfur. *Science* 266, 1973-1975.  
1797 doi:10.1126/science.11540246
- 1798 Canfield, D.E., Boudreau, B.P., Mucci, A., Gundersen, J.K. 1998. The early diagenetic  
1799 formation of organic sulfur in the sediments of Mangrove Lake, Bermuda. *Geochim.*  
1800 *Cosmochim. Acta* 62, 767-781.
- 1801 Canfield, D.E., Stewart, F.J., Thamdrup, B., De Brabandere, L., Dalsgaard, T., Delong, E.F.,  
1802 Revsbech, N.P., Ulloa, O., 2010. A cryptic sulfur cycle in oxygen-minimum-zone waters off  
1803 the Chilean coast. *Science*, 330,1375-1378. doi:10.1126/science.1196889
- 1804 Canuel, E.A., Freeman, K.H., Wakeham, S.G., 1997. Isotopic compositions of lipid biomarker  
1805 compounds in estuarine plants and surface sediments. *Limnol. Oceanogr.* 42, 1570-1583.  
1806 doi:10.4319/lo.1997.42.7.1570
- 1807 Carstens, D., Lehmann, M.F., Hofstetter, T.B., Schubert, C.J., 2013. Amino acid nitrogen  
1808 isotopic composition patterns in lacustrine sedimenting matter. *Geochim. Cosmochim. Acta*  
1809 121, 328-338. doi:10.1016/j.gca.2013.07.020
- 1810 Castañeda, I.S., Werne, J.P., Johnson, T.C., 2007. Wet and arid phases in the southeast

1811 African tropics since the Last Glacial Maximum. *Geology* 35, 823-826.  
 1812 doi:10.1130/G23916A.1

1813 Castañeda, I.S., Mulitza, S., Schefuß, E., Lopes dos Santos, R.A., Sinninghe Damsté, J.S.,  
 1814 Schouten, S., 2009. Wet phases in the Sahara/Sahel region and human migration patterns  
 1815 in North Africa. *Proc. Nat. Acad. Sci.* 106, 20159-20163. doi:10.1073/pnas.0905771106

1816 Castañeda, I.S. and Schouten, S., 2011. A review of molecular organic proxies for examining  
 1817 modern and ancient lacustrine environments. *Quat. Sci. Rev.* 30, 2851-2891.  
 1818 doi:10.1016/j.quascirev.2011.07.009

1819 Castañeda, I.S., Werne, J.P., Johnson, T.C., 2009. Influence of climate change on algal  
 1820 community structure and primary productivity of Lake Malawi (East Africa) from the Last  
 1821 Glacial Maximum to the present. *Limnol. Oceanogr.* 54, 2431-2447.  
 1822 doi:10.4319/lo.2009.54.6\_part\_2.2431

1823 Castañeda, I.S., Werne, J.P., Johnson, T.C., Powers, L.A., 2011. Organic geochemical  
 1824 records from Lake Malawi (East Africa) of the last 700 years, part II: Biomarker evidence for  
 1825 recent changes in primary productivity. *Palaeogeogr., Palaeoclim., Palaeoecol.* 303, 140-  
 1826 154. doi:10.1016/j.palaeo.2010.01.006

1827 Castoreno, A.B., Wang, Y., Stockinger, W., Jarzylo, L.A., Du, H., Pagnon, J.C., Shieh, E.C.,  
 1828 Nohturfft, A., 2005. Transcriptional regulation of phagocytosis-induced membrane  
 1829 biogenesis by sterol regulatory element binding proteins. *Proc. Nat. Acad. Sci.* 102, 13129-  
 1830 13134. doi:10.1073/pnas.0506716102

1831 Cernusak, L.A., Ubierna, N., Winter, K., Holtum, J.A.M., Marshall, J.D., Farquhar, G.D., 2013.  
 1832 Environmental and physiological determinants of carbon isotope discrimination in terrestrial  
 1833 plants. *New Phytol.* 200, 950-965. doi:10.1111/nph.12423

1834 Chikaraishi, Y., Naraoka, H., Poulson, S.R., 2004. Hydrogen and carbon isotopic  
 1835 fractionations of lipid biosynthesis among terrestrial (C3, C4 and CAM) and aquatic plants.  
 1836 *Phytochem.* 65, 1369-1381. doi:10.1016/j.phytochem.2004.03.036

1837 Chikaraishi, Y., Yamada, Y., Naraoka, H., 2005. Carbon and hydrogen isotopic compositions  
 1838 of sterols from riverine and marine sediments. *Limnol. Oceanogr.*, 50, 1763-1770.  
 1839 doi:10.4319/lo.2005.50.6.1763

1840 Chikaraishi, Y. and Naraoka, H., 2005.  $\delta^{13}\text{C}$  and  $\delta\text{D}$  identification of sources of lipid biomarkers  
 1841 in sediments of Lake Haruna (Japan). *Geochim. Cosmochim. Acta*, 69, 3285-3297.  
 1842 doi:10.1016/j.gca.2005.02.023

- 1843 Chikaraishi, Y. and Naraoka, H., 2006. Carbon and hydrogen isotope variation of plant  
1844 biomarkers in a plant–soil system. *Chem. Geol.*, 231, 190-202.  
1845 doi:10.1016/j.chemgeo.2006.01.026
- 1846 Chikaraishi, Y., Kashiyaama, Y., Ogawa, N.O., Kitazato, H., Ohkouchi, N., 2007. Metabolic  
1847 control of nitrogen isotope composition of amino acids in macroalgae and gastropods:  
1848 implications for aquatic food web studies. *Mar. Ecol. Prog. Ser.* 342, 85-90. doi:  
1849 10.3354/meps342085
- 1850 Chikaraishi, Y., Ogawa, N.O., Kashiyaama, Y., Takano, Y., Suga, H., Tomitani, A., Miyashita,  
1851 H., Kitazato, H., Ohkouchi, N., 2009. Determination of aquatic food-web structure based on  
1852 compound-specific nitrogen isotopic composition of amino acids. *Limnol. Oceanogr.*  
1853 *Methods* 7, 740-750. doi:10.4319/lom.2009.7.740
- 1854 Chikaraishi, Y., Ogawa, N.O., Ohkouchi, N., 2010. Further evaluation of the trophic level  
1855 estimation based on nitrogen isotopic composition of amino acids. In: Ohkouchi, N., Tayasu,  
1856 I., Koba, K. (eds.), *Earth, Life and Isotopes*. Kyoto University Press, Kyoto, pp. 37-51.
- 1857 Chivall, D., M'Boule, D., Sinke-Schoen, D., Sinninghe Damsté, J.S., Schouten, S., van der  
1858 Meer, M.T.J., 2014. The effects of growth phase and salinity on the hydrogen isotopic  
1859 composition of alkenones produced by coastal haptophyte algae. *Geochim. Cosmochim.*  
1860 *Acta* 140, 381-390. doi:10.1016/j.gca.2014.05.043
- 1861 Cisneros-Dozal, L.M., Huang, Y., Heikoop, J.M., Fawcett, P.J., Fessenden, J., Anderson,  
1862 R.S., Meyers, P.A., Larson, T., Perkins, G., Toney, J., Werne, J.P., Goff, F., WoldeGabriel,  
1863 G., Allen, C.D., Berke, M.A., 2014. Assessing the strength of the monsoon during the late  
1864 Pleistocene in southwestern United States. *Quat. Sci. Rev.* 103, 81-90.  
1865 doi:10.1016/j.quascirev.2014.08.022
- 1866 Cole, J.J. and Prairie, Y.T., 2009. Dissolved CO<sub>2</sub>. In: Likens, G.E. (ed.), *Encyclopedia of Inland*  
1867 *Waters*, vol. 2. Elsevier, Oxford, pp. 30-34.
- 1868 Collister, J.W. and Hayes, J., 1991. A preliminary study of the carbon and nitrogen isotopic  
1869 biogeochemistry of lacustrine sedimentary rocks from the Green River Formation. In: Tuttle,  
1870 M. (ed.), *Geochemical, Biogeochemical, and Sedimentological Studies of the Green River*  
1871 *Formation, Wyoming, Utah and Colorado*. U.S. Geol. Surv. Bull. 1973, pp. C1-C16.
- 1872 Collister, J.W., Summons, R.E., Lichtfouse, E., Hayes, J.M., 1992. An isotopic biogeochemical  
1873 study of the Green River oil-shale. *Org. Geochem.* 19, 265-276. doi:10.1016/0146-  
1874 6380(92)90042-V
- 1875 Collister, J.W., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific  $\delta^{13}\text{C}$



1876 analyses of leaf lipids from plants with differing carbon dioxide metabolisms. *Org. Geochem.*  
1877 21, 619-627. doi:10.1016/0146-6380(94)90008-6

1878 Coolen, M.J.L., Muyzer, G., Rijpstra, W.I.C., Schouten, S., Volkman, J.K., Sinninghe Damsté,  
1879 J.S., 2004a. Combined DNA and lipid analyses of sediments reveal changes in Holocene  
1880 haptophyte and diatom populations in an Antarctic lake. *Earth Planet. Sci. Lett.* 223, 225-  
1881 239. doi:10.1016/j.epsl.2004.04.014

1882 Coolen, M.J.L., Hopmans, E.C., Rijpstra, W.I.C., Muyzer, G., Schouten, S., Volkman, J.K.,  
1883 Sinninghe Damsté, J.S., 2004b. Evolution of the methane cycle in Ace Lake (Antarctica)  
1884 during the Holocene: response of methanogens and methanotrophs to environmental  
1885 change. *Org. Geochem.* 35, 1151-1167. doi:10.1016/j.orggeochem.2004.06.009

1886 Coolen, M.J.L., Talbot, H.M., Abbas, B.A., Ward, C., Schouten, S., Volkman, J.K., Sinninghe  
1887 Damsté, J.S., 2008. Sources for sedimentary bacteriohopanepolyols as revealed by 16S  
1888 rDNA stratigraphy. *Env. Microbiol.* 10, 1783-1803. doi:10.1111/j.1462-2920.2008.01601.x

1889 Coursolle, D., Lian, J., Shanklin, J., Zhao, H., 2015. Production of long chain alcohols and  
1890 alkanes upon coexpression of an acyl-ACP reductase and aldehyde-deformylating  
1891 oxygenase with a bacterial type-I fatty acid synthase in *E. coli*. *Mol. BioSyst.* 11, 2464.  
1892 doi:10.1039/c5mb00268k

1893 Craig, H. 1961. Isotopic variations in meteoric waters. *Science* 133, 1702-1703.  
1894 doi:10.1126/science.133.3465.1702

1895 Cranwell, P.A., 1981. Diagenesis of free and bound lipids in terrestrial detritus deposited in a  
1896 lacustrine sediment. *Org. Geochem.* 3, 79-89. doi:10.1016/0146-6380(81)90002-4

1897 Cranwell, P.A., 1985. Long-chain unsaturated ketones in recent lacustrine sediments.  
1898 *Geochim. Cosmochim. Acta* 49, 1545-1551. doi:10.1016/0016-7037(85)90259-5

1899 Cross, M.M., Manning, D.A.C., Bottrell, S.H., Worden, R.H., 2004. Thermochemical sulfate  
1900 reduction (TSR): experimental determination of reaction kinetics and implications of the  
1901 observed reaction rates for petroleum reservoirs. *Org. Geochem.* 35, 393-404.  
1902 doi:10.1016/j.orggeochem.2004.01.005

1903 Crossman, Z.M., McNamara, N., Parekh, N., Ineson, P., Evershed, R.P., 2001. A new method  
1904 for identifying the origins of simple and complex hopanoids in sedimentary materials using  
1905 stable isotope labeling with  $^{13}\text{CH}_4$  and compound specific stable isotope analyses. *Org.*  
1906 *Geochem.* 32, 359-364. doi:10.1016/S0146-6380(00)00178-9

1907 D'Andrea, W.J. and Huang, Y., 2005. Long chain alkenones in Greenland lake sediments: low

1908  $\delta^{13}\text{C}$  values and exceptional abundance. *Org. Geochem.* 36, 1234-1241.  
1909 doi:10.1016/j.orggeochem.2005.05.001

1910 D'Andrea, W.J., Lage, M., Martiny, J.B.H., Laatsch, A.D., Amaral-Zettler, L.A., Sogin, M.L.,  
1911 Huang, Y.S., 2006. Alkenone producers inferred from well-preserved 18S rDNA in Greenland  
1912 lake sediments. *J. Geophys. Res. Biogeosci.* 111. doi:10.1029/2005JG000121.

1913 Darling, W.G., Bath, A.H., Gibson, J.J., Rozanski, K., 2005. Isotopes in water, in: Leng, M.J.  
1914 (ed.), *Isotopes in Palaeoenvironmental Research*. Springer, Dordrecht, pp. 1-66.

1915 Davies, K.L., Pancost, R.D., Edwards, M.E., Walter Anthony, K.M., Langdon, P.G., Chaves  
1916 Torres, L., 2016. Diploptene  $\delta^{13}\text{C}$  values from contemporary thermokarst lake sediments  
1917 show complex spatial variation. *Biogeosci.* 13, 2611-2621. doi:10.5194/bg-13-2611-2016.

1918 Dawson, D., Grice, K., Wang, S.X., Alexander, R., Radke, J., 2004. Stable hydrogen isotopic  
1919 composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited  
1920 under various climatic conditions. *Org. Geochem.* 35, 189-197.  
1921 doi:10.1016/j.orggeochem.2003.09.004

1922 De Jonge, C., Stadnitskaia, A., Hopmans, E.C., Cherkashov, G., Fedotov, A., Sinninghe  
1923 Damsté, J.S., 2014. In situ produced branched glycerol dialkyl glycerol tetraethers in  
1924 suspended particulate matter from the Yenisei River, Eastern Siberia. *Geochim. Cosmochim.*  
1925 *Acta* 125, 476-491. doi:10.1016/j.gca.2013.10.031

1926 de Kluijver, A., Schoon, P.L., Downing, J.A., Schouten, S., Middelburg, J.J., 2014. Stable  
1927 carbon isotope biogeochemistry of lakes along a trophic gradient. *Biogeosci.* 11, 6265-6276.  
1928 doi:10.5194/bg-11-6265-2014

1929 DeLong, E.F., 1992. Archaea in coastal marine environments. *Proc. Natl. Acad. Sci.* 89, 5685-  
1930 5689. doi:10.1073/pnas.89.12.5685

1931 DeNiro, M.J. and Epstein, S., 1978. Influence of diet on the distribution of carbon isotopes in  
1932 animals. *Geochim. Cosmochim. Acta* 42, 495-506. doi.org/10.1016/0016-7037(78)90199-0

1933 Diefendorf, A. F. and Freimuth, E. J., 2017. Extracting the most from terrestrial plant-derived  
1934 *n*-alkyl lipids and their carbon isotopes from the sedimentary record: A review. *Org.*  
1935 *Geochem.* 103, 1-21. doi:10.1016/j.orggeochem.2016.10.016

1936 Diefendorf, A.F., Freeman, K.H., Wing, S.L., Graham, H.V., 2011. Production of *n*-alkyl lipids  
1937 in living plants and implications for the geologic past. *Geochim. Cosmochim. Acta* 75, 7472-  
1938 7485. doi:10.1016/j.gca.2011.09.028

1939 Edwards, T.W.D. and McAndrews, J.H. (1989). Paleohydrology of a Canadian Shield lake

- 1940 inferred from  $^{18}\text{O}$  in sediment cellulose. Can. J. Earth Sc. 26, 1850-185. doi:10.1139/e89-  
1941 158
- 1942 Eglinton, G. and Hamilton, R.J., 1967. Leaf epicuticular waxes. Science 156, 1322-1335. doi:  
1943 10.1126/science.156.3780.1322
- 1944 Eglinton, T.I. and Eglinton, G., 2008. Molecular proxies for paleoclimatology. Earth Planet. Sci.  
1945 Lett. 275, 1-16. doi:10.1016/j.epsl.2008.07.012
- 1946 Ehleringer, J.R., Hall, A.E., Farquhar, G.D., 1993. Stable isotopes and plant carbon/water  
1947 relations. Academic Press, San Diego, California, USA.
- 1948 Eickhoff, M., Birgel, D., Talbot, H.M., Peckmann, J., Kappler, A., 2013. Bacteriohopanoid  
1949 inventory of *Geobacter sulfurreducens* and *Geobacter metallireducens*. Org. Geochem. 58,  
1950 107-114. doi:10.1016/j.orggeochem.2013.02.013
- 1951 Eley, Y., Dawson, L., Pedentchouk, N., 2016. Investigating the carbon isotope composition  
1952 and leaf wax *n*-alkane concentration of C3 and C4 plants in Stiffkey saltmarsh, Norfolk, UK.  
1953 Org. Geochem. 96, 28-42. doi:10.1016/j.orggeochem.2016.03.005
- 1954 Eltgroth, M.L., Watwood, R.L., Wolfe, G.V., 2005. Production and cellular localization of  
1955 neutral long-chain lipids in the haptophyte algae *Isochrysis galbana* and *Emiliania huxleyi*. J.  
1956 Phycol. 41, 1000-1009. doi:10.1111/j.1529-8817.2005.00128.
- 1957 Elvert, M., Pohlman, J.W., Becker, K.W., Gaglioti, B., Henrichs, K.-U., Wooler, M.J., 2016.  
1958 Methane turnover and environmental change from Holocene lipid biomarker records in a  
1959 thermokarst lake in Arctic Alaska. Holocene 26, 1766-1777.
- 1960 Englebrecht, A.C. and Sachs, J.P., 2005. Determination of sediment provenance at drift sites  
1961 using hydrogen isotopes and unsaturation ratios in alkenones. Geochim. Cosmochim. Acta  
1962 69, 4253-4265. doi:10.1016/j.gca.2005.04.011
- 1963 Engels, S., Bakker, M.A.J., Bohncke, S.J.P., Cerli, C., Hoek, W.Z., Jansen, B., Peters, T.,  
1964 Renssen, H., Sachse, D., van Aken, J.M., van den Bos, V., van Geel, B., van Oostrom, R.,  
1965 Winkels, T., Wolma, M., 2016. Centennial-scale lake level lowstand at Lake Uddelermeer  
1966 (The Netherlands) indicates changes in moisture source region prior to the 2.8-kyr event.  
1967 Holocene 26, 1075-7091. doi:10.1177/0959683616632890
- 1968 Farquhar, J., Bao, H., Thiemens, M., 2000. Atmospheric influence of Earth's earliest sulfur  
1969 cycle. Science 289, 756-758. doi:10.1126/science.289.5480.756
- 1970 Farquhar, J., Johnston, D.T., Wing, B.A., Habicht, K.S., Canfield, D.E., Airieau, S., Thiemens,  
1971 M.H., 2003. Multiple sulphur isotopic interpretations of biosynthetic pathways: implications

- 1972 for biological signatures in the sulphur isotope record. *Geobiol.* 1, 27-36. doi:10.1046/j.1472-  
1973 4669.2003.00007.x
- 1974 Farquhar, J., Johnston, D.T., Wing, B.A., 2007. Implications of conservation of mass effects  
1975 on mass-dependent isotope fractionations: influence of network structure on sulfur isotope  
1976 phase space of dissimilatory sulfate reduction. *Geochim. Cosmochim. Acta* 71, 5862–5875.  
1977 doi:10.1016/j.gca.2007.08.028
- 1978 Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary  
1979 input of submerged/floating freshwater aquatic macrophytes. *Org. Geochem.* 31, 745-749.  
1980 doi:10.1016/S0146-6380(00)00081-4
- 1981 Freeman, K.H., Hayes, J.M., Trendel, J.-M., Albrecht, P., 1990. Evidence from carbon isotope  
1982 measurements for diverse origins of sedimentary hydrocarbons. *Nature* 343, 254-256.  
1983 doi:10.1038/343254a0
- 1984 Freeman, K.H. and Pancost, R.D., 2014. Biomarkers for terrestrial plants. In: Holland, H.D.  
1985 and Turekian, K.K. (eds.), *Treatise on Geochemistry*, 2nd edition, vol. 12. Elsevier,  
1986 Amsterdam, pp. 395-416. doi:10.1016/B978-0-08-095975-7.01028-7
- 1987 Freitas, F.S., Pancost, R.D., Arndt, S., 2017. The impact of alkenone degradation on  $U_{37}^{K'}$   
1988 paleothermometry: a model-derived assessment. *Paleoceanogr.* 32, 648-672.  
1989 doi:10.1002/2016PA003043
- 1990 Fry, B., Cox, J., Gest, H., Hayes, J., 1986. Discrimination between  $^{34}\text{S}$  and  $^{32}\text{S}$  during bacterial  
1991 metabolism of inorganic sulfur compounds. *J. Bacteriol.* 165, 328-330.
- 1992 Fry, B., 1986. Sources of carbon and sulfur nutrition for consumers in three meromictic lakes  
1993 of New York State. *Limnol. Oceanogr.*, 31, 79-88. doi: doi.org/10.4319/lo.1986.31.1.0079
- 1994 Fuhrman, J. and Davis, A., 1997. Widespread archaea and novel bacteria from the deep sea  
1995 as shown by 16S rRNA gene sequences. *Mar. Ecol. Prog. Ser.* 150, 275-285.  
1996 doi:10.3354/meps150275
- 1997 Fulton, J.M., Arthur, M.A., Thomas, B. Freeman, K.H., 2018. Pigment carbon and nitrogen  
1998 isotopic signatures in euxinic basins. *Geobiol.* 16, 429-445. doi:10.1111/gbi.12285
- 1999 Gaebler, O.H., Vitti, T.G., Vukmirovich, R., 1966. Isotope effects in metabolism of  $^{14}\text{N}$  and  $^{15}\text{N}$   
2000 from unlabeled dietary proteins. *Can J Biochem* 44, 1249-1257. doi:10.1139/o66-142
- 2001 Galimov, E.M., 1985. *The Biological Fractionation of Isotopes*. Academic Press, Orlando, pp.  
2002 261.
- 2003 Gamarra, B. and Kahmen, A., 2015. Concentrations and  $\delta^2\text{H}$  values of cuticular *n*-alkanes

- 2004 vary significantly among plant organs, species and habitats in grasses from an alpine and  
2005 temperate European grassland. *Oecologia* 178, 981-998. doi:10.1007/s00442-015-3278-6
- 2006 Gamarra, B., Sachse, D., Kahmen, A., 2016. Effects of leaf water evaporative  $^2\text{H}$ -enrichment  
2007 and biosynthetic fractionation on leaf wax *n*-alkane  $\delta^2\text{H}$  values in C3 and C4 grasses. *Plant,*  
2008 *Cell, Env.* 39, 2390-2403. doi: 10.1111/pce.12789
- 2009 Garcin, Y., Schefuß, E., Schwab, V.F., Garreta, V., Gleixner, G., Vincens, A., Todou, G., Séné,  
2010 O., Onana, J.-M., Achoundong, G., Sachse, D., 2014. Reconstructing C<sub>3</sub> and C<sub>4</sub> vegetation  
2011 cover using *n*-alkane carbon isotope ratios in recent lake sediments from Cameroon,  
2012 Western Central Africa. *Geochim. Cosmochim. Acta* 142, 482-500.  
2013 doi:10.1016/j.gca.2014.07.004
- 2014 Gelpi, E., Schneider, H., Mann, J., Oro, J., 1970. Hydrocarbons of geochemical significance  
2015 in microscopic algae. *Phytochem.* 9, 603-612. doi:10.1016/S0031-9422(00)85700-3
- 2016 Glazer, A.N., Apell, G.S., Hixson, C.S., Bryant, D.A., Rimon, S., Brown, D.M. 1976. Biliproteins  
2017 of cyanobacteria and Rhodophyta: homologous family of photosynthetic accessory  
2018 pigments. *Proc. Natl. Acad. Sci. USA* 73, 428-431. doi:10.1073/pnas.73.2.428
- 2019 Glibert, P.M., Wilkerson, F.P., Dugdale, R.C., Raven, J.A., Dupont, C.L., Leavitt, P.R., Parker,  
2020 A.E., Burkholder, J.M., Kana, T.M., 2016. Pluses and minuses of ammonium and nitrate  
2021 uptake and assimilation by phytoplankton and implications for productivity and community  
2022 composition, with emphasis on nitrogen-enriched conditions. *Limnol. Oceanogr.* 61, 165-  
2023 197. doi:10.1002/lno.10203
- 2024 Goericke, R., Montoya, J.P., Fry, B., 1994. Physiology of isotope fractionation in algae and  
2025 cyanobacteria. In: Lajtha, K. and Michener, B. (eds.), *Stable Isotopes in Ecology*. Blackwell  
2026 Scientific, Boston, pp. 187-221.
- 2027 Goldhaber, M.B. and Kaplan, I.R., 1980. Mechanisms of sulfur incorporation and isotope  
2028 fractionation during early diagenesis in sediments of the Gulf of California. *Mar. Chem.* 9,  
2029 95-143. doi:10.1016/0304-4203(80)90063-8
- 2030 Goodwin, T.W., 1976. Distribution of Carotenoids. In: Goodwin, T.W. (ed.), *Chemistry and*  
2031 *Biochemistry of Plant Pigments*, vol. 1, pp. 225-261. Academic Press, London.
- 2032 Goossens H., de Leeuw, J.W., Schenck, P.A., Brassell, S.C., 1984. Tocopherols as likely  
2033 precursors of pristane in ancient sediments and crude oils. *Nature* 312, 440-442.  
2034 doi:10.1038/312440a0
- 2035 Grantham, P.J. and Wakefield, L.L., 1988. Variations in the sterane carbon number

distributions of marine source rock derived crude oils through geological time. *Org. Geochem.* 12, 61-73. doi:10.1016/0146-6380(88)90115-5

Greenwood, P.F. and Summons, R.E., 2003. GC–MS detection and significance of crocetane and pentamethylicosane in sediments and crude oils. *Org. Geochem.* 34, 1211-1222. doi:10.1016/S0146-6380(03)00062-7

Greenwood, P.F., Mohammed, L., Grice, K., McCulloch, M.T., Schwark, L., 2018. The application of compound-specific sulfur isotopes to the oil-source rock correlation of Kurdistan petroleum. *Org. Geochem.* 117, 22-30. doi:10.1016/j.orggeochem.2017.11.016

Grice, K., Gibbison, R., Atkinson, J.E., Schwark, L., Eckardt, C.B., Maxwell, J.R., 1996a. Maleimides (1H-pyrrole-2,5-diones) as molecular indicators of anoxygenic photosynthesis in ancient water columns. *Geochim. Cosmochim. Acta* 60, 3913-3924. doi:10.1016/0016-7037(96)00199-8

Grice, K., Schaeffer, P., Schwark, L., Maxwell, J.R., 1996b. Molecular indicators of palaeoenvironmental conditions in an immature Permian shale (Kupferschiefer, Lower Rhine Basin, north-west Germany) from free and S-bound lipids. *Org. Geochem.* 25, 131-147. doi:10.1016/S0146-6380(96)00130-1

Grice, K., Schaeffer, P., Schwark, L., Maxwell, J.R., 1997. Changes in palaeoenvironmental conditions during deposition of the Permian Kupferschiefer (Lower Rhine Basin, northwest Germany) inferred from molecular and isotopic compositions of biomarker components. *Org. Geochem.* 26, 677-690. doi:10.1016/S0146-6380(97)00036-3

Grice, K., Schouten, S., Nissenbaum, A., Charrach, J., Sinninghe Damsté J.S., 1998. Isotopically heavy carbon in the C<sub>21</sub> to C<sub>25</sub> regular isoprenoids in halite-rich deposits from the Sdom Formation, Dead Sea Basin, Israel. *Org. Geochem.* 28, 349–359. doi:10.1016/S0146-6380(98)00006-0

Grice K., Twitchett R.J., Alexander R., Foster C.B., Looy C., 2005. A potential biomarker for the Permian-Triassic ecological crisis. *Earth Planet. Sci. Lett.* 236, 315-321. doi:10.1016/j.epsl.2005.05.008

Griffiths, M., 1978. Specific blue-green algal carotenoids in sediments of Esthwaite Water. *Limnol. Oceanogr.* 23, 777-784. doi:10.4319/lo.1978.23.4.0777

Guilizzoni, P., Lami, A., Marchetto, A., 1992. Plant pigment ratios from lake sediments as indicators of recent acidification in alpine lakes. *Limnol. Oceanogr.* 37, 1565-1569. doi:10.4319/lo.1992.37.7.1565

2068 Habicht, K.S. and Canfield, D.E., 1997. Sulfur isotope fractionation during bacterial sulfate  
2069 reduction in organic-rich sediments. *Geochim. Cosmochim. Acta* 61, 5351-5361.  
2070 doi:10.1016/S0016-7037(97)00311-6

2071 Habicht, K.S. and Canfield, D.E., 2001. Isotope fractionation by sulfate-reducing natural  
2072 populations and the isotopic composition of sulfide in marine sediments. *Geology* 29, 555-  
2073 558. doi:10.1130/0091-7613(2001)029<0555:IFBSRN>2.0.CO;2

2074 Habicht, K.S., Canfield, D.E., and Rethmeier, J., 1998. Sulfur isotope fractionation during  
2075 bacterial reduction and disproportionation of thiosulfate and sulfite. *Geochim. Cosmochim.*  
2076 *Acta* 62, 2585-2595. doi:10.1016/S0016-7037(98)00167-7.

2077 Hartgers, W.A., Koopmans, M.P., Sinninghe Damsté, J.S., De Leeuw, J.W., 1993.  
2078 Sedimentary evidence for a diaromatic carotenoid with an unprecedented aromatic  
2079 substitution pattern. *J. Chem. Soc. Chem. Comm.* 23, 1715-1716. doi:  
2080 10.1039/C39930001715

2081 Harvey, H.W., 1940. Nitrogen and phosphorus required for the growth of phytoplankton. *J.*  
2082 *Mar. Biol. Assoc.* 24, 115-123. doi:10.1017/S0025315400054485

2083 Harvey, H.W., 1953. Synthesis of organic nitrogen and chlorophyll by *Nitzschia closterium*. *J.*  
2084 *Mar. Biol. Assoc.* 31, 477-487. doi:10.1017/S0025315400011632

2085 Hayes, J.M., 2001. Fractionation of carbon and hydrogen isotopes in biosynthetic processes.  
2086 *Rev. Mineral. Geochem.* 43, 225-277. doi:10.2138/gsrmg.43.1.225

2087 Hayes, J.M., Popp, B.N., Takigiku, R., Johnson, M.W., 1989. An isotopic study of  
2088 biogeochemical relationships between carbonates and organic carbon in the Greenhorn  
2089 Formation. *Geochim. Cosmochim. Acta* 53, 2961-2972. doi:10.1016/0016-7037(89)90172-5

2090 Hayes, J.M., Strauss, H., Kaufman, A.J., 1999. The abundance of <sup>13</sup>C in marine organic matter  
2091 and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800  
2092 Ma. *Chem. Geol.* 161, 103-125. doi:10.1016/S0009-2541(99)00083-2

2093 Hedges, J.I., 1992. Global biogeochemical cycles - Progress and problems. *Mar. Chem.* 39,  
2094 67-93. doi:10.1016/0304-4203(92)90096-S

2095 Hedges, J.I. and Keil, R.G., 1995. Sedimentary organic matter preservation - An assessment  
2096 and speculative synthesis. *Mar. Chem.* 49, 81-115. doi:10.1016/0304-4203(95)00008-F

2097 Hepp, J., Tuthorn, M., Zech, R., Mügler, I., Schlütz, F., Zech, W., Zech, M., 2015.  
2098 Reconstructing lake evaporation history and the isotopic composition of precipitation by a  
2099 coupled  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  biomarker approach. *J. Hydrol.* 529, 622-631.

2100 Hershberger, K.L., Barns, S.M., Reysenbach, A.-L., Dawson, S.C., Pace, N.R., 1996. Wide  
2101 diversity of Crenarchaeota. *Nature* 384, 420-420. doi:10.1038/384420a0

2102 Heyng, A.M., Mayr, C., Lücke, A., Wissel, H., Striewski, B., 2014. Late Holocene hydrologic  
2103 changes in northern New Zealand inferred from stable isotope values of aquatic cellulose in  
2104 sediments from Lake Pupuke. *J. Paleolim.* 51, 485-497. doi:10.1007/s10933-014-9769-3

2105 Heyng, A.M., Mayr, C., Lücke, A., Moschen, R., Wissel, H., Striewski, B., Bauersachs, T.,  
2106 2015. Middle and Late Holocene paleotemperatures reconstructed from oxygen isotopes  
2107 and GDGTs of sediments from Lake Pupuke, New Zealand. *Quat. Int.* 374, 3-14.  
2108 doi:10.1016/j.quaint.2014.12.040

2109 Higgins, M.B., Robinson, R.S., Carter, S.J., Pearson, A., 2010. Evidence from chlorin nitrogen  
2110 isotopes for alternating nutrient regimes in the Eastern Mediterranean Sea: *Earth Planet.*  
2111 *Sci. Let.* 290, no. 1–2, p. 102-107, doi: 10.1016/j.epsl.2009.12.009.

2112 Hilkert, A.W., Douthitt, C.B., Schlüter, H.J., Brand, W.A., 1999. Isotope ratio monitoring gas  
2113 chromatography/mass spectrometry of D/H by high temperature conversion isotope ratio  
2114 mass spectrometry. *Rapid Commun. Mass Spectrom.* 13, 1226-1230.  
2115 doi:10.1002/(SICI)1097-0231(19990715)13:13<1226::AID-RCM575>3.0.CO;2-9

2116 Hinrichs, K.U., Hayes, J.M., Sylva, S.P., Brewer, P.G., DeLong, E.F., 1999. Methane-  
2117 consuming archaeobacteria in marine sediments. *Nature* 398, 802-805. doi:10.1038/19751

2118 Hinrichs, K.U., Schneider, R.R., Müller, P.J., Rullkötter, J., 1999. A biomarker perspective on  
2119 paleoproductivity variations in two Late Quaternary sediment sections from the Southeast  
2120 Atlantic Ocean. *Org. Geochem.* 30, 341-366. doi:10.1016/S0146-6380(99)00007-8

2121 Hinrichs, K.-U., Summons, R.E., Orphan, V., Sylva, S.P., Hayes, J.M., 2000. Molecular and  
2122 isotopic analysis of anaerobic methane-oxidizing communities in marine sediments. *Org.*  
2123 *Geochem.* 31, 1685-1701. doi:10.1016/S0146-6380(00)00106-6

2124 Hoefs, J., 2004. *Stable Isotope Geochemistry*, 5th edition. Springer, Berlin, pp. 244.

2125 Hoefs, M., Schouten, S., De Leeuw, J.W., King, L.L., Wakeham, S.G., Sinninghe Damsté,  
2126 J.S., 1997. Ether lipids of planktonic archaea in the marine water column. *Appl. Environ.*  
2127 *Microbiol.* 63, 3090-3095.

2128 Hoering, T.C. and Ford, H.T., 1960. The isotope effect in the fixation of nitrogen by  
2129 *Azotobacter*. *J. Am. Chem. Soc.*, 82, 376-8. doi:10.1021/ja01487a031

2130 Hollander, D.J. and Smith, M.E., 2001. Microbially mediated carbon cycling as a control on  
2131 the  $\delta^{13}\text{C}$  of sedimentary carbon in eutrophic Lake Mendota (USA): New models for



2132 interpreting isotopic excursions in the sedimentary record. *Geochim. Cosmochim. Acta* 65,  
2133 4321-4337. doi:10.1016/S0016-7037(00)00506-8

2134 Hollander, D.J., Sinninghe Damsté, J.S., Hayes, J.M., De Leeuw, J.W., Huc, A.Y., 1993.  
2135 Molecular and bulk isotopic analyses of organic matter in marls of the Mulhouse Basin  
2136 (Tertiary, Alsace, France). *Org. Geochem.* 20, 1253-1263. doi:10.1016/0146-  
2137 6380(93)90013-2

2138 Holtvoeth, J. Rushworth, D., Imeri, A., Cara, M., Vogel, H., Wagner, T., Wolff, G.A., 2016.  
2139 Improved end-member characterisation of modern organic matter pools in the Ohrid Basin  
2140 (Albania, Macedonia) and evaluation of new palaeoenvironmental proxies. *Biogeosci.* 13,  
2141 795-816. doi:10.5194/bg-13-795-2016

2142 Holtvoeth, J., Vogel, H., Valsecchi, V., Lindhorst, K., Schouten, S., Wagner, B., Wolff, G.A.,  
2143 2017. Linear and non-linear responses of vegetation and soils to glacial-interglacial climate  
2144 change in a Mediterranean refuge. *Sci. Rep.* 7, 8121. doi:10.1038/s41598-017-08101-y

2145 Hou, J., D'Andrea, W.J., MacDonald, D., Huang, Y., 2007. Hydrogen isotopic variability in leaf  
2146 waxes among terrestrial and aquatic plants around Blood Pond, Massachusetts (USA). *Org.*  
2147 *Geochem.* 38, 977-984. doi:10.1016/j.orggeochem.2006.12.009

2148 Huang, X., Pancost, R.D., Xue, J., Gu, Y., Evershed, R.P., Xie, S., 2018. Response of carbon  
2149 cycle to drier conditions in the mid-Holocene in central China. *Nature Communications*  
2150 9:1369. DOI: 10.1038/s41467-018-03804-w.

2151 Huang, Y., Murray, M., Eglinton, G., 1995. Sacredicene, a novel monocyclic C<sub>33</sub> hydrocarbon  
2152 from sediment of Sacred Lake, a tropical freshwater lake, Mount Kenya. *Tetrahedron Letters*  
2153 36, 5973-5976. doi:10.1016/0040-4039(95)01156-C

2154 Huang, Y., Lockheart, M.J., Logan, G.A., Eglinton, G., 1996. Isotope and molecular evidence  
2155 for the diverse origins of carboxylic acids in leaf fossils and sediments from the Miocene  
2156 Lake Clarkia deposit, Idaho, U.S.A.. *Org. Geochem.* 24, 289-299. doi:10.1016/0146-  
2157 6380(96)00030-7

2158 Huang, Y.S., Street-Perrott, F.A., Perrot, R.A., Metzger, P., Eglinton, G., 1999. Glacial-  
2159 interglacial environmental changes inferred from molecular and compound-specific  $\delta^{13}\text{C}$   
2160 analyses of sediments from Sacred Lake, Mt. Kenya. *Geochim. Cosmochim. Acta* 63, 1383-  
2161 1404. doi:10.1016/S0016-7037(99)00074-5

2162 Huang, Y., Street-Perrott, F.A., Metcalfe, S.E., Brenner, M., Moreland, M., Freeman, K.H.,  
2163 2001. Climate change as the dominant control on glacial-interglacial variations in C<sub>3</sub> and C<sub>4</sub>  
2164 plant abundance. *Science* 293, 1647-1651. doi:10.1126/science.1060143

2165 Huang, Y., Shuman, B., Wang, Y., Webb III, T., 2004. Hydrogen isotope ratios of individual  
 2166 lipids in lake sediments as novel tracers of climatic and environmental change: a surface  
 2167 sediment test. *J. Paleolim.* 31, 363-375. doi:10.1023/B:JOPL.0000021855.80535.13

2168 Huang, Y., Shuman, B., Wang, Y., Webb III, T., Grimm, E.C., Jacobson, G.L. Jr., 2006.  
 2169 Climatic and environmental controls on the variation of C3 and C4 plant abundances in  
 2170 central Florida for the past 62,000 years. *Palaeogeogr., Palaeoclim., Palaeoecol.* 237, 428-  
 2171 435. doi:10.1016/j.palaeo.2005.12.014

2172 Jaeschke, A., Ziegler, M., Hopmans, E.C., Reichart, G.J., Lourens, L.J., Schouten, S.,  
 2173 Sinninghe Damsté, J.S., 2009. Molecular fossil evidence for anaerobic ammonium oxidation  
 2174 in the Arabian Sea over the last glacial cycle. *Paleoceanogr.* 24, PA2202-1-PA2202-11.  
 2175 doi:10.1029/2008PA001712

2176 Jaffé, R., Cabrera, A., Najje, N., Carvajal-Chitty, H., 1996. Organic biogeochemistry of a  
 2177 hypereutrophic tropical, freshwater lake – Part 1: particle associated and dissolved lipids.  
 2178 *Org. Geochem.* 25, 227-240. doi:10.1016/S0146-6380(96)00114-3

2179 Jahnke, L.L., Summons, R.E., Hope, J.M., Des Marais, D.J., 1999. Carbon isotopic  
 2180 fractionation in lipids from methanotrophic bacteria II: The effects of physiology and  
 2181 environmental parameters on the biosynthesis and isotopic signatures of biomarkers.  
 2182 *Geochim. Cosmochim. Acta* 63, 79-93. doi:10.1016/S0016-7037(98)00270-1

2183 Jetter, R., Schaffer, S., Riederer, M., 2000. Leaf cuticular waxes are arranged in chemically  
 2184 and mechanically distinct layers: evidence from *Prunus laurocerasus* L. *Plant Cell Env.* 23,  
 2185 619-628. doi:10.1046/j.1365-3040.2000.00581.x

2186 Jochmann, M.A. and Schmidt, T.C., 2012. *Compounds-specific Stable Isotope Analysis*. The  
 2187 Royal Society of Chemistry, Cambridge, pp. 250.

2188 Johnson, T.C., Werne, J.P., Brown, E.T., Abbott, A., Berke, M., Steinman, B.A., Halbur, J.,  
 2189 Contreras, S., Grosshuesch, S., Deino, A., Lyons, R.P., Scholz, C.A., Schouten, S.,  
 2190 Sinninghe Damsté, J.S., 2016, A progressively wetter climate in southern East Africa over  
 2191 the past 1.3 million years. *Nature* 537, 220-224. doi:10.1038/nature19065

2192 Johnston, D.T., Farquhar, J., Wing, B.A., Kaufman, A., Canfield, D.E., Habicht, K.S., 2005.  
 2193 Multiple sulfur isotope fractionations in biological systems: a case study with sulfate reducers  
 2194 and sulfur disproportionators. *Am. J. Sci.* 305, 645-660. doi:10.2475/ajs.305.6-8.645

2195 Johnston, D.T., Farquhar, J., Canfield, D.E. 2007. Sulfur isotope insights into microbial sulfate  
 2196 reduction: when microbes meet models. *Geochim. Cosmochim. Acta* 71, 3929-3947.  
 2197 doi:10.1016/j.gca.2007.05.008

- 2198 Johnston, D.T., Farquhar, J., Habicht, K., Canfield, D.E. 2008. Sulphur isotopes and the  
2199 search for life: strategies for identifying sulphur metabolisms in the rock record and beyond.  
2200 *Geobiol.* 6, 425–435. doi:10.1111/j.1472-4669.2008.00171.x
- 2201 Jones, D.M., Carter, J.F., Eglinton, G., Jumeau, E.J., Fenwick, C.S., 1991. Determination of  
2202  $\delta^{13}\text{C}$  values of sedimentary straight chain and cyclic alcohols by gas chromatography/isotope  
2203 ratio mass spectrometry. *Biol. Mass Spectr.* 20, 641-646. doi:10.1002/bms.1200201009
- 2204 Jones G.J., Nichols P.D., Shaw P.M., 1994. Analysis of microbial sterols and hopanoids. In:  
2205 Goodfellow M. and O'Donnell A.G (eds.), *Chemical Methods in Prokaryotic Systematics*.  
2206 Wiley, Chichester, pp.163-195
- 2207 Jørgensen, B.B. (1978). A comparison of methods for the quantification of bacterial sulfate  
2208 reduction in coastal marine sediments. *Geomicrobiol. J.* 1, 29-47.  
2209 doi:1080/01490457809377722
- 2210 Jørgensen, B.B., Böttcher, M.E., Lüschen, H., Neretin, L.N., Volkov, I.I., 2004. Anaerobic  
2211 methane oxidation and a deep  $\text{H}_2\text{S}$  sink generate isotopically heavy sulfides in Black Sea  
2212 sediments. *Geochim. Cosmochim. Acta*, 68, 2095-2118. doi:10.1016/j.gca.2003.07.017
- 2213 Kahmen, A., Schefuß, E., Sachse, D., 2013a. Leaf water deuterium enrichment shapes leaf  
2214 wax *n*-alkane  $\delta\text{D}$  values of angiosperm plants I: Experimental evidence and mechanistic  
2215 insights. *Geochim. Cosmochim. Acta* 111, 39-49. doi:10.1016/j.gca.2012.09.003.
- 2216 Kahmen, A., Hoffmann, B., Schefuß, E., Arndt, S.K., Cernusak, L.A., West, J.B., Sachse, D.,  
2217 2013b. Leaf water deuterium enrichment shapes leaf wax *n*-alkane  $\delta\text{D}$  values of angiosperm  
2218 plants II: Observational evidence and global implications. *Geochim. Cosmochim. Acta* 111,  
2219 50-63. doi:10.1016/j.gca.2012.09.004
- 2220 Kaneko, M., Kitajima, F., Naraoka, H., 2011. Stable hydrogen isotope measurement of  
2221 archaeal ether-bound hydrocarbons. *Org. Geochem.* 42, 166-172.  
2222 doi:10.1016/j.orggeochem.2010.11.002
- 2223 Kaplan, I. and Rittenberg, S., 1964. Microbiological fractionation of sulphur isotopes. *J. Gen.*  
2224 *Microbiol.* 34, 195-212. doi:10.1099/00221287-34-2-195
- 2225 Kaplan, I.R., Emery, K.O., Rittenberg, S.C., 1963. The distribution and isotopic abundance of  
2226 sulphur in recent marine sediments off southern California. *Geochim. Cosmochim. Acta* 27,  
2227 297-331. doi:10.1016/0016-7037(63)90074-7
- 2228 Karner, M.B., DeLong, E.F., Karl, D.M., 2001. Archaeal dominance in the mesopelagic zone  
2229 of the Pacific Ocean. *Nature* 409, 507-510. doi:10.1038/35054051

- 2230 Kasprak, A.H., Sepúlveda, J., Price-Waldman, R., Williford, K.H., Schoepfer, S.D., Haggart,  
2231 J.W., Ward, P.D., Summons, R.E., Whiteside, J.H., 2015. Episodic photic zone euxinia in the  
2232 northeastern Panthalassic Ocean during the end-Triassic extinction. *Geology* 43, 307-310.  
2233 doi:10.1130/G36371.1
- 2234 Kharasch, N., (ed.) 2013. *Organic Sulfur Compounds*. Elsevier.
- 2235 Khezami, L., Chetouani, B., Tauk, B., Capart, R., 2005. Production and characterisation of  
2236 activated carbon from wood components in powder: Cellulose, lignin, xylan. *Powder Tech.*  
2237 157, 48-56. doi:10.1016/j.powtec.2005.05.009
- 2238 Kimble, B.J., Maxwell, J.R., Philp, R.P. Eglinton, G., Albrecht, P., Ensminger, A., Arpino, P.,  
2239 Ourisson, G., 1974. Tri- and tetraterpenoid hydrocarbons in the Messel oil shale. *Geochim.*  
2240 *Cosmochim. Acta* 38, 1165-1181. doi:10.1016/0016-7037(74)90011-8
- 2241 Kitamura, E., Kotajima, T., Sawada, K., Suzuki, I., Shiraiwa, Y., 2018. Cold-induced metabolic  
2242 conversion of haptophyte di- to tri-unsaturated C<sub>37</sub> alkenones used as palaeothermometer  
2243 molecules. *Sci. Rep.* 8, 2196. doi:10.1038/s41598-018-20741-2
- 2244 Knoll, A.H., Summons, R.E., Waldbauer, J.R., Zumberge, J.E., 2007. The geological  
2245 succession of primary producers in the oceans. In: Falkowski, P.D. and Knoll, A.H. (eds.),  
2246 *Evolution of Primary Producers in the Sea*, Elsevier, Oxford, pp.133-163.
- 2247 Kodner, R.B., Pearson, A., Summons, R.E., Knoll, A.H., 2008. Sterols in red and green algae:  
2248 quantification, phylogeny, and relevance for the interpretation of geologic steranes. *Geobiol.*  
2249 6, 411-420. doi:10.1111/j.1472-4669.2008.00167.x
- 2250 Kohn, M.J., 2010. Carbon isotope compositions of terrestrial C<sub>3</sub> plants as indicators of  
2251 (paleo)ecology and (paleo)climate. *Proc. Nat. Acad. Sci.* 101, 19691–19695.  
2252 doi:10.1073/pnas.1004933107
- 2253 Konecky, B.L., Russell, J.M., Johnson, T.C., Brown, E.T., Berke, M.A., Werne, J.P., Huang,  
2254 Y., 2011. Atmospheric circulation patterns during late Pleistocene climate changes at Lake  
2255 Malawi, Africa. *Earth Planet. Sci. Lett.* 312, 318-326. doi:10.1016/j.epsl.2011.10.020
- 2256 Könneke, M., Lipp, J.S., Hinrichs, K.-U., 2012. Carbon isotope fractionation by the marine  
2257 ammonia-oxidizing archaeon *Nitrosopumilus maritimus*. *Org. Geochem.* 48, 21-24.  
2258 doi:10.1016/j.orggeochem.2012.04.007
- 2259 Kool, D.M., Talbot, H.M., Rush, D., Ettwig, K., Sinninghe Damsté, J.S., 2014. Rare  
2260 bacteriohopanepolyols as markers for an autotrophic, intra-aerobic methanotroph. *Geochim.*  
2261 *Cosmochim. Acta* 136, 114-125. doi:10.1016/j.gca.2014.04.002

- 2262 Koopmans, M.P., Köster, J., van Kaam-Peters, H.M.E., Kenig, F., Schouten, S., Hartgers,  
2263 W.A., de Leeuw, J.W., Sinninghe Damsté, J.S., 1996. Diagenetic and catagenetic products  
2264 of isorenieratene: Molecular indicators for photic zone anoxia. *Geochim. Cosmochim. Acta*  
2265 60, 4467-4496. doi:10.1016/S0016-7037(96)00238-4
- 2266 Körner, C. H., Farquhar, G. D., Wong, S. C., 1991. Carbon isotope discrimination by plants  
2267 follows latitudinal and altitudinal trends. *Oecologia* 88, 30-40. doi:10.1007/BF00328400
- 2268 Koyama, M., Sugiyama, J., Itoh, T., 1997. Systematic survey on crystalline features of algal  
2269 celluloses. *Cellulose* 4, 147-160. doi:10.1023/A:101842760
- 2270 Kraal, P., Burton, E.D., Bush, R.T., 2013. Iron monosulfide accumulation and pyrite formation  
2271 in eutrophic estuarine sediments. *Geochim. Cosmochim. Acta*, 122, 75-88.  
2272 doi:10.1016/j.gca.2013.08.013
- 2273 Krouse, H.R., Viau, C.A., Eliuk, L.S. (1988) Chemical and isotopic evidence of thermo-  
2274 chemical sulfate reduction by light hydrocarbon gases in deep carbonate reservoirs. *Nature*  
2275 333, 415-419. doi:10.1038/333415a0
- 2276 Kümmel, S., Starke, R., Chen, G., Musat, F., Richnow, H.H., Vogt, C., 2016. Hydrogen isotope  
2277 fractionation as a tool to identify aerobic and anaerobic PAH biodegradation. *Environ. Sci.*  
2278 *Technol.* 50, 3091-3100. doi:10.1021/acs.est.5b04819
- 2279 Kuypers, M.M.M., Blokker, P., Erbacher, J., Kinkel, H., Pancost, R.D., Schouten, S., Sinninghe  
2280 Damsté, J.S., 2001. Massive expansion of marine archaea during a mid-Cretaceous oceanic  
2281 anoxic event. *Science* 293, 92–95. doi:10.1126/science.1058424
- 2282 Kuypers, M.M.M., Blokker, P., Hopmans, E.C., Kinkel, H., Pancost, R.D., Schouten, S.,  
2283 Sinninghe Damsté, J.S., 2002. Archaeal remains dominate marine organic matter from the  
2284 early Albian oceanic anoxic event 1b. *Palaeogeogr., Palaeoclim., Palaeoecol.* 185, 211-234.  
2285 doi:10.1016/S0031-0182(02)00301-2
- 2286 Ladd, S.N., Dubois, N., Schubert C.J., 2017. Interplay of community dynamics, temperature,  
2287 and productivity on the hydrogen isotope signatures of lipid biomarkers. *Biogeosci.* 14, 3979-  
2288 3994. doi:10.5194/bg-14-3979-2017.
- 2289 Lamb, A.L., Wilson, G.P., Leng, M.J., 2006. A review of coastal palaeoclimate and relative  
2290 sea-level reconstructions using  $\delta^{13}\text{C}$  and C/N ratios in organic material. *Earth-Sci. Rev.* 75  
2291 29-57. doi:10.1016/j.earscirev.2005.10.003
- 2292 Langworthy, T.A., 1977. Long-chain diglycerol tetraethers from *Thermoplasma acidophilum*.  
2293 *Biochim. Biophys. Acta BBA - Lipids Lipid Metab.* 487, 37-50. doi:10.1016/0005-

2294 2760(77)90042-X

2295 Langworthy, T.A., 1982. Lipids of *Thermoplasma*. Meth. Enzym., 88, 396-406.  
 2296 doi:10.1016/0076-6879(82)88055-5

2297 Langworthy, T.A., Smith, P.F., Mayberry, W.R., 1972. Lipids of *Thermoplasma acidophilum*.  
 2298 J. Bacteriol. 112, 1193-1200.

2299 Larsen, T., Bach, L.T., Salvatelli, R., Wang, Y.V., Andersen, N., Ventura, M., McCarthy, M.D.,  
 2300 2015. Assessing the potential of amino acid <sup>13</sup>C patterns as a carbon source tracer in marine  
 2301 sediments: effects of algal growth conditions and sedimentary diagenesis. Biogeosci. 12,  
 2302 4979-4992. doi: 10.5194/bg-12-4979-2015

2303 Laws, E.A., Popp, B.N., Bidigare, R.R., Kennicutt, M.C., Macko, S.A., 1995. Dependence of  
 2304 phytoplankton carbon isotopic composition on growth rate and [CO<sub>2</sub>]<sub>aq</sub>: Theoretical  
 2305 considerations and experimental results. Geochim. Cosmochim. Acta 59, 1131-1138.  
 2306 doi:10.1016/0016-7037(95)00030-4

2307 De Leeuw, J.W., Rijpstra, W.I.C., Schenck, P.A., Volkman, J.K., 1983. Free, esterified and  
 2308 residual bound sterols in Black Sea Unit I sediments. Geochim. Cosmochim. Acta 47, 455-  
 2309 465. doi:10.1016/0016-7037(83)90268-5

2310 Leininger, S., Urich, T., Schlöter, M., Schwark, L., Qi, J., Nicol, G.W., Prosser, J.I., Schuster,  
 2311 S.C., Schleper, C., 2006. Archaea predominate among ammonia-oxidizing prokaryotes in  
 2312 soils. Nature 442, 806-809. doi:10.1038/nature04983

2313 Lengeler, J.W., Drew, G., Schlegel, H.G., 1999. Biology of the Prokaryotes. Blackwell Science,  
 2314 New York, pp. 984.

2315 Lengger, S.K., Lipsewiers, Y.A., de Haas, H., Sinninghe Damsté, J.S., Schouten, S., 2014.  
 2316 Lack of <sup>13</sup>C-label incorporation suggests low turnover rates of thaumarchaeal intact polar  
 2317 tetraether lipids in sediments from the Iceland shelf. Biogeosci. 11, 201-216. doi:10.5194/bg-  
 2318 11-201-2014

2319 Lengger, S.K., Sutton, P.A., Rowland, S.J., Hurley, S.J., Pearson, A., Naafs, B.D.A., Dang,  
 2320 X., Inglis, G.N., Pancost, R.D., 2018. Archaeal and bacterial glycerol dialkyl glycerol  
 2321 tetraether (GDGT) lipids in environmental samples by high temperature-gas chromatography  
 2322 with flame ionisation and time-of-flight mass spectrometry detection. Org. Geochem. 121,  
 2323 10-21. doi:10.1016/j.orggeochem.2018.03.012

2324 Li, J. Philp, R.P., Pu, F., Allen, J., 1996. Long-chain alkenones in Qinghai Lake sediments.  
 2325 Geochim. Cosmochim. Acta 60, 235-241. doi:10.1016/0016-7037(95)00389-4

- 2326 Li, C., Sessions, A.L., Kinnaman, F.S., Valentine, D.L., 2009. Hydrogen-isotopic variability in  
2327 lipids from Santa Barbara Basin sediments. *Geochim. Cosmochim. Acta* 73, 4803-4823.  
2328 doi:10.1016/j.gca.2009.05.056
- 2329 Liaaen-Jensens, S., 1979. Marine carotenoids. In: Scheuer, P. (ed.), *Marine Natural*  
2330 *Productions, Chemical and Biological Perspectives*, vol. 2, pp. 2-73, Academic Press,  
2331 London.
- 2332 Lucas, W.J., 1983. Photosynthetic assimilation of exogenous  $\text{HCO}_3^-$  by aquatic plants. *Annu.*  
2333 *Rev. Plant Physiol.* 34, 71-104. doi:10.1146/annurev.pp.34.060183.000443
- 2334 Luo, Y.-H., Sternberg, L., Suda, S., Kumazawa, S., Mitsui, A., 1991. Extremely low D/H ratios  
2335 of photoproduced hydrogen by cyanobacteria. *Plant Cell Physiol.* 32, 897-900.
- 2336 MacGregor, B.J., Moser, D.P., Alm, E.W., Nealson, K.H., Stahl, D.A., 1997. Crenarchaeota in  
2337 Lake Michigan sediment. *Appl. Environ. Microbiol.* 63, 1178-1181.
- 2338 Mackenzie, A.S., Brassell, S.C., Eglinton, G., Maxwell, J.R., 1982. Chemical fossils: the  
2339 geological fate of steroids. *Science* 217, 491-504. doi:10.1126/science.217.4559.491
- 2340 Magill, C.R., Ashley, G.M., Freeman, K.H., 2013. Ecosystem variability and early human  
2341 habitats in eastern Africa, *Proc. Nat. Acad. Sci.* 110, 1167-1174.  
2342 doi:10.1073/pnas.1206276110
- 2343 Mansour, M.P., Volkman, J.K., Jackson, A.E., Blackburn, S.I., 1999. The fatty acid and sterol  
2344 composition of five marine dinoflagellates. *J. Phycol.* 35, 710-720. doi:10.1046/j.1529-  
2345 8817.1999.3540710.x
- 2346 Marlowe, I.T., Brassell, S.C., Eglinton, G., Green, J.C., 1984. Long chain unsaturated ketones  
2347 and esters in living algae and marine sediments. *Org. Geochem.* 6, 135-141.  
2348 doi:10.1016/0146-6380(84)90034-2
- 2349 Maslen, E., Grice, K., Gale, J.D., Hallmann, C., Horsfield, B., 2009. Crocetane: A potential  
2350 marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age.  
2351 *Org. Geochem.* 40, 1-11. doi:10.1016/j.orggeochem.2008.10.005
- 2352 Maslen, E., Grice, K., Dawson, D., Wang, S., Horsfield, B., 2012. Stable hydrogen isotopes of  
2353 isoprenoids and *n*-alkanes as a proxy for estimating the thermal history of sediments through  
2354 geological time. In: Harris, N.B. and Peters, K.E (eds.) *Analyzing the Thermal History of*  
2355 *Sedimentary Basins: Methods and Case Studies*. SEPM Spec. Publ. 103, SEPM, Tulsa, pp.  
2356 29-44. doi:10.2110/sepmssp.103
- 2357 Matsumoto, G., Torii, T., Hanya, T., 1982. High abundance of algal 24-ethylcholesterol in

2358 Antarctic lake sediment. *Nature* 299, 52-54. doi:10.1038/299052a0

2359 Matsumoto, G.I., Fujimura, C., Minoura, K., Takamatsu, N., Takemura, T., Hayashi, S., Shichi,  
 2360 K., Kawai, T., 2003. Paleoenvironmental changes in the Eurasian continental interior during  
 2361 the last 12 million years derived from organic components in sediment cores (BDP-96 and  
 2362 BDP-98) from Lake Baikal. In: Kashiwaya, K. (ed.), *Long Continental Records from Lake*  
 2363 *Baikal*, Springer, Tokyo, pp. 75-94.

2364 Matthews, D.E. and Hayes, J.M., 1978. Isotope-ratio-monitoring gas chromatography-mass  
 2365 spectrometry. *Anal. Chem.* 50, 1465-1473. doi: 10.1021/ac50033a022

2366 Matys, E.D., Sepulveda, J., Pantoja, S., Lange, C.B., Caniupan, M., Lamy, F., Summons, R.E.,  
 2367 2017. Bacteriohopaneoplyols along redox gradients in the Humboldt Current System off  
 2368 northern Chile. *Geobiol.* 15, 844-857. doi:10.1111/gbi.12250

2369 Maxwell, J.R., Douglas, A.G., Eglinton, G., McCormick, A., 1968. The Botryococcenes—  
 2370 hydrocarbons of novel structure from the alga *Botryococcus braunii*, Kützing. *Phytochem.* 7,  
 2371 2157-2171. doi:10.1016/S0031-9422(00)85672-1

2372 Mayr, C., Lücke, A., Wagner, S., Wissel, H., Ohlendorf, C., Haberzettl, T., Oehlerich, M.,  
 2373 Schäbitz, F., Wille, M., Zhu, J., Zolitschka, B., 2013. Intensified southern hemisphere  
 2374 westerlies regulated atmospheric CO<sub>2</sub> during the last deglaciation. *Geology* 41, 831-834.  
 2375 doi:10.1130/G34335.1

2376 Mayr, C., Laprida, C., Lücke, A., Martín, R.S., Massaferro, J., Ramón-Mercau, J., Wissel, H.,  
 2377 2015. Oxygen isotope ratios of chironomids, aquatic macrophytes and ostracods for lake-  
 2378 water isotopic reconstructions - Results of a calibration study in Patagonia. *J. Hydrol.* 529,  
 2379 600-607. doi:10.1016/j.jhydrol.2014.11.001

2380 M'boule, D., Chivall, D., Sinke-Schoen, D., Sinninghe Damsté, J.S., Schouten, S., van der  
 2381 Meer, M.T.J., 2014. Salinity dependent hydrogen isotope fractionation in alkenones  
 2382 produced by coastal and open ocean haptophyte algae. *Geochim. Cosmochim. Acta* 130,  
 2383 126-135. doi:10.1016/j.gca.2014.01.029

2384 McCarthy, M.D., Benner, R., Lee, C., Fogel, M.L., 2007. Amino acid nitrogen isotopic  
 2385 fractionation patterns as indicators of heterotrophy in plankton, particulate, and dissolved  
 2386 organic matter. *Geochim. Cosmochim. Acta* 71, 4727-4744. doi:10.1016/j.gca.2007.06.061

2387 McClelland, J.W. and Montoya, J.P., 2002. Trophic relationships and the nitrogen isotopic  
 2388 composition of amino acids in plankton. *Ecology* 83, 2173-2180. doi:10.1890/0012-  
 2389 9658(2002)083[2173:TRATNI]2.0.CO;2



- 2390 Mendez-Millan, M, Dignac, M.-F., Rumpel, C, Derenne, S., 2010. Can cutin and suberin  
2391 biomarkers be used to trace shoot and root-derived organic matter? A molecular and isotopic  
2392 approach. *Biogeochem.* 106, 23-38. doi:10.1007/s10533-010-9407.
- 2393 Menzel, D., van Bergen, P.F., Schouten, S., 2003. Reconstruction of changes in export  
2394 productivity during Pliocene sapropel deposition: a biomarker approach. *Palaeogeogr.,*  
2395 *Palaeoclim., Palaeoecol.* 190, 273-287. doi:10.1016/S0031-0182(02)00610-7
- 2396 Metzger, P. and Largenau, C., 1999. Chemicals of *Botryococcus braunii*. In: Cohen Z (ed.)  
2397 Chemicals from Microalgae. London: Taylor and Francis.
- 2398 Metzger, P., Casadevall, E., Pouet, M.J., Pouet, Y., 1985. Structures of some botryococcenes  
2399 - branched hydrocarbons from the B race of the green-alga *Botryococcus braunii*.  
2400 *Phytochem.* 24, 2995-3002. doi:10.1016/0031-9422(85)80043-1
- 2401 Meyers, P.A. and Ishiwatari, R., 1993. Lacustrine organic geochemistry - an overview of  
2402 indicators of organic matter sources and diagenesis in lake sediments. *Org. Geochem.* 20,  
2403 867-900. doi:10.1016/0146-6380(93)90100-P
- 2404 Meyers, P.A. and Ishiwatari, R., 1995. Organic matter accumulation records in lake sediments.  
2405 In: Lerman, A., Imboden, D.M., Gat, J.R. (eds.), *Physics and Chemistry of Lakes*. Springer,  
2406 Berlin, Heidelberg, pp. 279-328.
- 2407 Meyers, P.A. and Teranes, J.L., 2001. Sediment Organic Matter. In: Last, W.M. and Smol,  
2408 J.P. (eds.), *Tracking Environmental Change Using Lake sediments*, vol. 2, *Physical and*  
2409 *Geochemical Methods*. Kluwer Academic Publishers, Dordrecht, pp. 239-270.
- 2410 Millar, A.M. and Kunst, L., 1997. Very-long-chain fatty acid biosynthesis is controlled through  
2411 the expression and specificity of the condensing enzyme. *Plant Journal* 12, 121-131.  
2412 doi:10.1046/j.1365-313X.1997.12010121.x
- 2413 Minagawa, M. and Wada, E., 1984. Stepwise enrichment of  $^{15}\text{N}$  along food chains: Further  
2414 evidence and the relation between  $\delta^{15}\text{N}$  and animal age. *Geochim. Cosmochim. Acta* 48,  
2415 1135-1140. doi:10.1016/0016-7037(84)90204-7
- 2416 Moldowan, J.M., 1984.  $\text{C}_{30}$ -steranes, novel markers for marine petroleums and sedimentary  
2417 rocks. *Geochim. Cosmochim. Acta*, 48, 2767-2768. doi:10.1016/0016-7037(84)90321-1
- 2418 Molina, I., Bonaventure, G., Ohlrogge, J., Pollard, M., 2006. The lipid polyester composition of  
2419 *Arabidopsis thaliana* and *Brassica napus* seeds. *Phytochem.* 67, 2597-2610. doi:  
2420 10.1016/j.phytochem.2006.09.011
- 2421 Morana, C., Borges, A.V., Roland, F.A.E., Darchambeau, F., Descy, J.-P., Bouillon, S., 2015.

2422 Methanotrophy within the water column of a large meromictic tropical lake (Lake Kivu, East  
2423 Africa). *Biogeosci.* 12, 2077-2088. doi:10.5194/bg-12-2077-2015

2424 Mügler, I., Sachse, D., Werner, M., Xu, B., Wu, G., Yao, T., Gleixner, G., 2008. Effect of lake  
2425 evaporation on  $\delta D$  values of lacustrine *n*-alkanes: A comparison of Nam Co (Tibetan  
2426 Plateau) and Holzmaar (Germany). *Org. Geochem.* 39, 711-729.  
2427 doi:10.1016/j.orggeochem.2008.02.008

2428 Naeher, S., Smittenberg, R.H., Gilli, A., Kirilova, E.P., Lotter, A.F., Schubert, C.M., 2012.  
2429 Impact of recent lake eutrophication on microbial community changes as revealed by high  
2430 resolution lipid biomarkers in Rotsee (Switzerland). *Org. Geochem.* 49, 86-95.  
2431 doi:10.1016/j.orggeochem.2012.05.014

2432 Naeher, S., Schaeffer, P., Adam, P., Schubert, C.J., 2013. Maleimides in recent sediments –  
2433 Using chlorophyll degradation products for palaeoenvironmental reconstructions. *Geochim.*  
2434 *Cosmochim. Acta* 119, 248-263. doi:10.1016/j.gca.2013.06.004

2435 Naeher, S., Niemann, H., Peterse, F., Smittenberg, R.H., Zigah, P.K., Schubert, C.M., 2014.  
2436 Tracing the methane cycle with lipid biomarkers in Lake Rotsee (Switzerland). *Org.*  
2437 *Geochem.* 66, 174-181. doi:10.1016/j.orggeochem.2013.11.002

2438 Nelson, D.B. and Sachs, J.P., 2013. Concurrent purification of sterols, triterpenols and  
2439 alkenones from sediments for hydrogen isotope analysis using high performance liquid  
2440 chromatography. *Org. Geochem.* 64, 19-28. doi:10.1016/j.orggeochem.2013.09.005

2441 Nelson, D.B. and Sachs, J.P., 2014. The influence of salinity on D/H fractionation in alkenones  
2442 from saline and hypersaline lakes in continental North America. *Org. Geochem.* 66, 38-47.  
2443 doi:10.1016/j.orggeochem.2013.10.013

2444 Nelson, D.B. and Sachs, J.P., 2016. Galápagos hydroclimate of the Common Era from paired  
2445 microalgal and mangrove biomarker  $^2H/^1H$  values. *Proc. Nat. Acad. Sci.*, 113, 3476-3481.  
2446 doi:10.1073/pnas.1516271113

2447 Neunlist, S. and Rohmner, M., 1985. Novel hopanoids from the methylotrophic bacteria  
2448 *Methylococcus capsulatus* and *Methylomonas methanica* (22S)-35-aminobacteriohopane-  
2449 30,31,32,33,34-pentol and (22S)-35-amino-3 $\beta$ -methylbacteriohopane-30,31,32,33,34-  
2450 pentol. *Biochem. J.* 231, 635-639.

2451 Neunlist, S., Rodier, C., Llopiz, P., 2002. Isotopic biogeochemistry of the lipids in recent  
2452 sediments of Lake Bled (Slovenia) and Baldeggersee (Switzerland). *Org. Geochem.* 33,  
2453 1183-1195. doi:10.1016/S0146-6380(02)00085-2

2454 Nichols, J.E., Walcott, M., Bradley, R., Pilcher, J., Huang, Y., 2009. Quantitative assessment  
2455 of precipitation seasonality and summer surface wetness using ombrotrophic sediments from  
2456 an Arctic Norwegian peatland. *Quat. Res.* 72, 443-451. doi: 10.1016/j.yqres.2009.07.007

2457 Niemann, H. and Elvert, M., 2008. Diagnostic lipid biomarker and stable carbon isotope  
2458 signatures of microbial communities mediating the anaerobic oxidation of methane with  
2459 sulphate. *Org. Geochem.* 39, 1668-1677. doi:10.1016/j.orggeochem.2007.11.003

2460 Nieto-Moreno, V., Rohrmann, A., van der Meer, M.T.J., Sinninghe Damsté, J.S., Sachse, D.,  
2461 Tofelde, S., Niedermeyer, E.M., Strecker, M.R., Mulch, A., 2016. Elevation-dependent  
2462 changes in *n*-alkane  $\delta D$  and soil GDGTs across the South Central Andes. *Earth Planet. Sci.*  
2463 *Lett.* 453, 234-242. doi:10.1016/j.epsl.2016.07.049

2464 Oakes, A.M. and Hren, M.T., 2016. Temporal variations in the  $\delta D$  of leaf *n*-alkanes from four  
2465 riparian plant species. *Org. Geochem.* 97, 122-130. doi:10.1016/j.orggeochem.2016.03.010

2466 Ocampo, R., Callot, H.J., Albrecht, P., 1985. Occurrence of bacteriopetroporphyrins in oil  
2467 shale. *J. Chem. Soc., Chem. Commun.*, 200-201. doi:10.1039/C39850000200

2468 O'Connell, T.C., 2017. 'Trophic' and 'source' amino acids in trophic estimation: a likely  
2469 metabolic explanation. *Oecologia* 184, 317-326. doi:10.1007/s00442-017-3881-9

2470 Oduro, H., Kamyshny, A., Guo, W., Farquhar, J., 2011. Multiple sulfur isotope analysis of  
2471 volatile organic sulfur compounds and their sulfonium precursors in coastal marine  
2472 environments. *Mar. Chem.* 124, 78-89. doi:10.1016/j.marchem.2010.12.004

2473 Oduro, H., Van Alstyne, K.L., Farquhar, J., 2012. Sulfur isotope variability of oceanic DMSP  
2474 generation and its contributions to marine biogenic sulfur emissions. *PNAS* 109, 9012-9016.  
2475 doi:10.1073/pnas.1117691109

2476 Oduro, H., Kamyshny Jr, A., Zerkle, A.L., Li, Y., Farquhar, J., 2013. Quadruple sulfur isotope  
2477 constraints on the origin and cycling of volatile organic sulfur compounds in a stratified  
2478 sulfidic lake. *Geochim. Cosmochim. Acta* 120, 251-262. doi:10.1016/j.gca.2013.06.039

2479 Ohkouchi, N., Kahiya, Y., Chikaraishi, Y., Ogawa, N.O., Tada, R., Kitazato, H., 2006.  
2480 Nitrogen isotopic composition of chlorophylls and porphyrins in geological samples as tools  
2481 for reconstructing paleoenvironment. *Geochim. Cosmochim. Acta* 70, A452,  
2482 doi:10.1016/j.gca.2006.06.911.

2483 Ohkouchi, N., Chikaraishi, Y., Close, H.G., Fry, B., Larsen, T., Madigan, D.J., McCarthy, M.D.,  
2484 McMahon, K.W., Nagata, T., Naito, Y.I., Ogawa, N.O., Popp, B.N., Steffan, S., Takano, Y.,  
2485 Tayasu, I., Wyatt, A.S.J., Yamaguchi, Y.T., Yokoyama, Y., 2017. Advances in the application

2486 of amino acid nitrogen isotopic analysis in ecological and biogeochemical studies, *Org.*  
2487 *Geochem.* 113, 150-174. doi:10.1016/j.orggeochem.2017.07.009

2488 O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. *BioSci.* 38, 328-336.  
2489 doi:10.2307/1310735

2490 Ono, S., Wing, B., Johnston, D., Farquhar, J., Rumble, D., 2006. Mass-dependent  
2491 fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur  
2492 biogeochemical cycles. *Geochim. Cosmochim. Acta* 70, 2238-2252.  
2493 doi:10.1016/j.gca.2006.01.022

2494 Orphan, V.J., Hinrichs, K.-U., Ussler, III, W., Paull, C.K., Taylor, L.T., Sylva, S.P., Hayes, J.M.,  
2495 Delong, E.F., 2001. Comparative analysis of methane-oxidizing Archaea and sulfate-  
2496 reducing bacteria in anoxic marine sediments. *Appl. Environ. Microbiol.* 67, 1922-1934.  
2497 doi:10.1128/AEM.67.4.1922-1934.2001

2498 Osborne, K. A., Gray, N.D., Sherry, A., Leary, P., Mejeha, O., Bischoff, J., Rush, D., Sidgwick,  
2499 F.R., Birgel, D., Kalyuzhnaya, M.G., Talbot, H.M., 2017. Methanotroph-derived  
2500 bacteriohopanepolyol signatures as a function of temperature related growth, survival, cell  
2501 death and preservation in the geological record. *Env. Microbiol. Rep.* 9, 492–500.  
2502 doi:10.1111/1758-2229.12570

2503 Osburn, M.R., Dawson, K.S., Fogel, M.L., Sessions, A.L., 2016. Fractionation of hydrogen  
2504 isotopes by sulfate- and nitrate-reducing bacteria. *Front. Microbiol.* 7, 1166.  
2505 doi:10.3389/fmicb.2016.01166

2506 Otto, A. and Simpson, M.J., 2005. Degradation and preservation of vascular plant-derived  
2507 biomarkers in grassland and forest soils from Western Canada. *Biogeochem.* 74, 377-409.  
2508 doi:10.1007/s10533-004-5834-8

2509 Pancost, R.D. and Sinninghe Damsté, J.S., 2003. Carbon isotopic compositions of prokaryotic  
2510 lipids as tracers of carbon cycling in diverse settings. *Chem. Geol.* 195, 29-58.  
2511 doi:10.1016/S0009-2541(02)00387-X

2512 Pancost, R.D. and Pagani, M., 2006. Controls on the carbon isotopic compositions of lipids in  
2513 marine environments. In: *Marine Organic Matter: Biomarkers, Isotopes and DNA*, Springer,  
2514 Berlin, pp. 209-249.

2515 Pancost, R.D., Freeman, K.H., Wakeham, S.G., 1999. Controls on the carbon-isotope  
2516 compositions of compounds in Peru surface waters. *Org. Geochem.* 30, 319-340.  
2517 doi:10.1016/S0146-6380(99)00004-2

2518 Pancost, R.D, Crawford, N., Maxwell, J.R., 2002. Molecular evidence for basin-scale photic  
 2519 zone euxinia in the Permian Zechstein Sea. *Chem. Geol.* 188, 217-227. doi:10.1016/S0009-  
 2520 2541(02)00104-3

2521 Pancost, R.D., Sinninghe Damsté, J.S., de Lint, S., van der Maarel, M.J.E.C., Gottschal, J.C.,  
 2522 The Medinaut Shipboard Scientific Party, 2000. Biomarker evidence for widespread  
 2523 anaerobic methane oxidation in mediterranean sediments by a consortium of methanogenic  
 2524 archaea and bacteria. *Appl. Environ. Microbiol.* 66, 1126–1132.  
 2525 doi:10.1128/AEM.66.3.1126-1132.2000

2526 Paoli, M., Marles-Wright, J., Smith, A., 2002. Structure-function relationships in heme-  
 2527 proteins. *DNA Cell Biol.* 21, 271-280. doi:10.1089/104454902753759690

2528 Parkin, T.B. and Brock, T.D., 1980. The effects of light quality on the growth of phototrophic  
 2529 bacteria in lakes. *Archives Microbiol.* 125, 19-27. doi:10.1007/BF00403193

2530 Pärn, J., Affolter, S., Ivask, J., Johnson, S.C., Kirsimäe, K., Leuenberger, M., Martma, T.,  
 2531 Raidla, V., Schloemer, S., Sepp, H., Vaikmäe, R., Walraevens, K., 2018. Redox zonation  
 2532 and organic matter oxidation in palaeogroundwater of glacial origin from the Baltic Artesian  
 2533 Basin. *Chem. Geol.* 488, 149-161. doi:10.1016/j.chemgeo.2018.04.027

2534 Passier, H.F. Böttcher, M.E., De Lange, G.J. 1999. Sulphur enrichment in organic matter of  
 2535 Eastern Mediterranean sapropels: A study of sulphur isotope partitioning. *Aq. Geochem.* 5,  
 2536 99-118. doi:10.1023/A:1009676107330

2537 Pearson, A., Budin, M., Brocks, J.J., 2003. Phylogenetic and biochemical evidence for sterol  
 2538 synthesis in the bacterium *Gemmata obscuriglobus*. *Proc. Nat. Acad. Sci.* 100, 15352-15357.  
 2539 doi:10.1073/pnas.2536559100

2540 Pearson A., Flood Page, S.R., Jorgenson, T.L., Fischer, W.W., Higgins, M.B., 2007. Novel  
 2541 hopanoid cyclases in the environment. *Environm. Microbiol.* 9, 2175-2188.  
 2542 doi:10.1111/j.1462-2920.2007.01331.x

2543 Pearson, A., Hurley, S.J., Walter, S.R.S., Kusch, S., Lichtin, S., Zhang, Y.G., 2016. Stable  
 2544 carbon isotope ratios of intact GDGTs indicate heterogeneous sources to marine sediments.  
 2545 *Geochim. Cosmochim. Acta* 181, 18-35. doi:10.1016/j.gca.2016.02.034

2546 Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The Biomarker Guide*. Cambridge  
 2547 University Press.

2548 Peterson, B.J. and Fry, B., 1987. Stable isotopes in ecosystem studies. *Ann. Rev. Ecol. Syst.*  
 2549 18, 293-320. doi:10.1146/annurev.es.18.110187.001453

2550 Pfenning, 1978. General physiology and ecology of photosynthetic bacteria. In: Clayton, R.K.  
 2551 and Sistrom, W.R. (eds.) Photosynthetic Bacteria, Plenum Press, pp. 3-16.

2552 Pickering M.D. and Keely, B.J., 2011. Low temperature abiotic formation of  
 2553 mesopyrophaeophorbide a from pyrophaeophorbide a under conditions simulating anoxic  
 2554 natural environments. *Geochim. Cosmochim. Acta* 75, 533-540.  
 2555 doi:10.1016/j.gca.2010.10.020

2556 Pollard, M., Beisson, F., Li, Y., Ohlrogge, J., 2008. Building lipid barriers: biosynthesis of cutin  
 2557 and suberin. *Trends Plant Sci.* 13, 236-246. doi: 10.1016/j.tplants.2008.03.003

2558 Popp, B.N., Takigiku, R., Hayes, J.M., Louda, J.W., Baker, E.W., 1989. The post-Paleozoic  
 2559 chronology and mechanism of <sup>13</sup>C depletion in primary marine organic matter. *Am. J. Sci.*,  
 2560 289, 436-454. doi:10.2475/ajs.289.4.436

2561 Popp, B.N., Kenig, F., Wakeham, S.G., Laws, E.A., Bidigare, R.R., 1998. Does growth rate  
 2562 affect ketone unsaturation and intracellular carbon isotopic variability in *Emiliania huxleyi*?  
 2563 *Paleoceanogr.* 13, 35-41. doi:10.1029/97PA02594

2564 Popp, B.N., Trull, T., Kenig, F., Wakeham, S.G., Rust, T.M., Tilbrook, B., Griffiths, B., Wright,  
 2565 S.W., Marchant, H.J., Bidigare, R.R., Laws, E.A., 1999. Controls on the carbon isotopic  
 2566 composition of Southern Ocean phytoplankton. *Global Biogeochem. Cycles* 13, 827-843.  
 2567 doi:10.1029/1999GB900041

2568 Popper, Z.A., Michel, G., Hervé, C., Domozych, D.S., Willats, W.G.T., Tuohy, M.G., Kloareg,  
 2569 B., Stengel, D.B., 2011. Evolution and diversity of plant cell walls: from algae to flowering  
 2570 plants. *Ann Rev Plant Biol* 62, 567-590. doi:10.1146/annurev-arplant-042110-103809

2571 Poralla, K., Härtner, T., Kannenberg, E., 1984. Effect of temperature and pH on the hopanoid  
 2572 content of *Bacillus acidocaldarius*. *FEMS Microbiol. Let.* 23, 253-256. doi:10.1111/j.1574-  
 2573 6968.1984.tb01073.x

2574 Post, W.M., Emanuel, W.R., Zinke, P.J., Stangenberger, A.G., 1977. Soil carbon pools and  
 2575 world life zones. *Nature* 298, 156-159. doi:10.1038/298156a0

2576 Powers, L.A., Werne, J.P., Johnson, T.C., Hopmans, E.C., Sinninghe Damsté, J.S., Schouten,  
 2577 S., 2004. Crenarchaeotal membrane lipids in lake sediments: A new paleotemperature proxy  
 2578 for continental paleoclimate reconstruction? *Geology* 32, 613. doi:10.1130/G20434.1

2579 Prahl, F., Herbert, T., Brassell, S.C., Ohkouchi, N., Pagani, M., Repeta, D., Rosell-Melé, A.,  
 2580 Sikes, E., 2000. Status of alkenone paleothermometer calibration: Report from Working  
 2581 Group 3. *Geochem. Geophys. Geosyst.* 1, paper no. 2000GC000058.

2582      doi:10.1029/2000GC000058

2583      Prahl, F.G., Cowie, G.L., De Lange, G.J., Sparrow, M.A., 2003. Selective organic matter  
 2584      preservation in “burn-down” turbidites on the Madeira Abyssal Plain. *Paleoceanogr.* 18.  
 2585      doi:10.1029/2002PA000853

2586      Prins, H.B.A. and Elzenga, J.T.M., 1989. Bicarbonate utilization: Function and mechanism.  
 2587      *Aquatic Bot.* 34, 59-83. doi:10.1016/0304-3770(89)90050-8

2588      Quandt, L., Gottschalk, G., Ziegler, H., Stichler, W., 1977. Isotope discrimination by  
 2589      photosynthetic bacteria. *FEMS Microbiology Letters* 1, 125-128, doi:10.1111/j.1574-  
 2590      6968.1977.tb00596.x

2591      Rach, O., Brauer, A., Wilkes, H., Sachse, D., 2014. Delayed hydrological response to  
 2592      Greenland cooling at the onset of the Younger Dryas in western Europe. *Nat. Geosci.* 7, 109-  
 2593      113. doi:10.1038/ngeo2053

2594      Rach O., Engels, S., Kahmen, A., Brauer, A., Martín-Puertas, C., van Geel, B., Sachse D.,  
 2595      2017. Hydrological and ecological changes in western Europe between 3200 and 2000 cal  
 2596      years BP derived from lipid biomarker  $\delta D$  values in Lake Meerfelder Maar sediments.  
 2597      *Quatern. Sci. Rev.* 172, 44-54. doi:10.1016/j.quascirev.2017.07.019

2598      Raghoebarsing, A.A, Smolders, A.J., Schmid, M.C., Ripstra, I.C., 2005. Methanotrophic  
 2599      symbionts provide carbon for photosynthesis. *Nature* 436; doi:10.1038/nature03802

2600      Rampen, S.W., Schouten, S., Abbas, B., Panoto, F.E., Muyzer, G., Campbell, C.N., Fehling,  
 2601      J., Sinninghe Damsté, J.S., 2007. On the origin of 24-norcholestanes and their use as age-  
 2602      diagnostic biomarkers. *Geology* 35, 419-422. doi:10.1130/G23358A.1

2603      Rampen, S.W., Abbas, B.A., Schouten, S., Sinninghe Damsté, J.S., 2010. A comprehensive  
 2604      study of sterols in marine diatoms (Bacillariophyta): implications for their use as tracers for  
 2605      diatom productivity. *Limnol. Oceanogr.* 55, 91-105. doi:10.4319/lo.2010.55.1.0091

2606      Rao, Z., Jia, G., Qiang, M., Zhao, Y., 2014. Assessment of the difference between mid- and  
 2607      long chain compound specific  $\delta D_{n\text{-alkanes}}$  values in lacustrine sediments as a paleoclimatic  
 2608      indicator. *Org. Geochem.* 76, 104-117. doi:10.1016/j.orggeochem.2014.07.015

2609      Raven, M.R., Adkins, J.F., Werne, J.P., Lyons, T.W., Sessions, A.L., 2015. Sulfur isotopic  
 2610      composition of individual organic compounds from Cariaco Basin sediments. *Org. Geochem.*  
 2611      80, 53-59. doi:10.1016/j.orggeochem.2015.01.002

2612      Redfield, A.C., 1958. The biological control of chemical factors in the environment. *Am. Sci.*,  
 2613      46, 205-211.

2614 Rees, C.E., Jenkins, W.J., Monster, J., 1978. The sulfur isotope geochemistry of ocean water  
2615 sulfate. *Geochim. Cosmochim. Acta* 42, 377-381. doi:10.1016/0016-7037(78)90268-5

2616 Reiffarth, D.G., Petticrew, E.L., Lobb, D.A., 2016. Sources of variability in fatty acid (FA)  
2617 biomarkers in the application of compound-specific stable isotopes (CSSIs) to soil and  
2618 sediment fingerprinting and tracing: A review. *Sci. Total Environ.* 565, 8-27.  
2619 doi:10.1016/j.scitotenv.2016.04.137

2620 Rho, J. and Litsky, W., 1979. Cellulose production by planktonic algae in lacustrine  
2621 environments. *Hydrobiologia* 66, 249-258. doi:10.1007/BF00020907

2622 Ricci, J.N., Coleman, M.L., Welander, P.V., Sessions, A.L., Summons, R.E., Spear, J.R.,  
2623 Newman, D.K., 2014. Diverse capacity for 2-methylhopanoid production correlates with a  
2624 specific ecological niche. *ISME J* 8:675-684. doi:10.1038/ismej.2013.191

2625 Ricci, J.N., Morton, R., Kulkarni, G., Summers, M.L., Newman, D.K. 2017. Hopanoids play a  
2626 role in stress tolerance and nutrient storage in the cyanobacterium *Nostoc punctiforme*.  
2627 *Geobiol.* 15, 173-183. doi:10.1111/gbi.12204

2628 Richey, J.N. and Sachs, J.P., 2016. Precipitation changes in the western tropical Pacific over  
2629 the past millennium. *Geology* 44, 671-674. doi:10.1130/G37822.1

2630 Riedinger, N., Brunner, B., Krastel, S., Arnold, G.L., Wehrmann, L.M., Formolo, M.J., Beck,  
2631 A., Bates, S.M., Henkel, S., Kasten, S., Lyons, T.W., 2017. Sulfur cycling in an iron oxide-  
2632 dominated, dynamic marine depositional system: The Argentine continental margin. *Front.*  
2633 *Earth Sci.* 5, 33. doi:10.3389/feart.2017.00033

2634 Roden, J.S, Lin, G., Ehleringer, J.R, 2000. A mechanistic model for interpretation of hydrogen  
2635 and oxygen isotope ratios in tree-ring cellulose. *Geochim. Cosmochim. Acta* 64, 21-35.  
2636 doi:10.1016/S0016-7037(99)00195-7

2637 Rodrigo, M.A., Vicente, E., Miracle, M.R., 2000. The role of light and concentration gradients  
2638 in the vertical stratification and seasonal development of phototrophic bacteria in a  
2639 meromictic lake. *Archives Hydrobiol.* 148, 533-548. doi:10.1127/archiv-  
2640 hydrobiol/148/2000/533

2641 Rohmer, M., Knani, M., Simonin, P., Sutter, B., Sahm, H., 1993. Isoprenoid biosynthesis in  
2642 bacteria: a novel pathway for the early steps leading to isopentenyl diphosphate. *Biochem.*  
2643 *J.* 295, 517-524. doi:10.1042/bj2950517

2644 Rohmer, M., Bouvier, P., Ourisson, G., 1979. Molecular evolution of biomembranes: structural  
2645 equivalents and phylogenetic precursors of sterols. *Proc. Nat. Acad. Sci.*, 76, 847-851.



doi:10.1073/pnas.76.2.847

Rohmer M., Bouvier-Nave, P., Ourisson G., 1984. Distribution of hopanoid triterpenes in prokaryotes. *J. Gen. Microbiol.* 130,1137-1150. doi:10.1099/00221287-130-5-1137

Romero-Viana, L., Kienel, U., Wilkes, H., Sachse, D., 2013. Growth-dependent hydrogen isotopic fractionation of algal lipid biomarkers in hypersaline Isabel Lake (México). *Geochim. Cosmochim. Acta* 106, 490-500. doi:10.1016/j.gca.2012.12.017

Ronkainen, T., McClymont, E.L., Välranta, M., Tuittila, E.-S., 2013. The *n*-alkane and sterol composition of living fen plants as a potential tool for palaeoecological studies. *Org. Geochem.* 59, 1-9. doi:10.1016/j.orggeochem.2013.03.005

Rontani, J.-F., Prahl, F.G., Volkman, J.K., 2006. Re-examination of the double bond position in alkenones and derivatives: biosynthetic implications. *J. Phycol.* 42, 800-813. doi:10.1111/j.1529-8817.2006.00251.x

Ross, P., Mayer, R., Benziman, M., 1991. Cellulose biosynthesis and function in bacteria. *Microbiol. Rev.* 55, 35-58.

Rozanski, K., Klisch, M. A., Wachniew, P., Gorczyca, Z., Goslar, T., Edwards, T. W. D., Shemesh, A., 2010. Oxygen-isotope geothermometers in lacustrine sediments: New insights through combined  $\delta^{18}\text{O}$  analyses of aquatic cellulose, authigenic calcite and biogenic silica in Lake Gosciaz, central Poland. *Geochim. Cosmochim. Acta* 74, 2957-2969. doi:10.1016/j.gca.2010.02.026

Rush, D., Sinninghe Damsté, J.S., Poulton, S.W., Thamdrup, B., Garside, A.L., González, J.A., Schouten, S., Jetten, M.S.M., Talbot, H.M., 2014. Anaerobic ammonium-oxidising bacteria: A biological source of the bacteriohopanetetrol stereoisomer in marine sediments. *Geochim. Cosmochim. Acta.* 140, 50-64. doi:10.1016/j.gca.2014.05.014

Rush, D., Osborne, K.A., Birgel, D., Kappler, A., Hirayama, H., Peckmann, J., Poulton, S.W., Nickel, J.C., Mangelsdorf, K., Kalyuzhnaya, M., Sidgwick, F.R., Talbot, H.M., 2016. The bacteriohopanepolyol inventory of novel aerobic methane oxidising bacteria reveals new biomarker signatures of aerobic methanotrophy in marine systems. *PLoS One* 11, e0165635. doi:10.1371/journal.pone.0165635

Sachs, J.P. and Repeta, D.J., 1999. Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events: *Science* 286, 2485-2488, doi:10.1126/science.286.5449.2485.

Sachs, J.P. and Repeta, D.J., 2000. The purification of chlorins from marine particles and

2678 sediments for nitrogen and carbon isotopic analysis. *Org. Geochem.* 31, 317-329,  
 2679 doi:10.1016/S0146-6380(99)00149-7.

2680 Sachs, J.P., Sachse, D., Smittenberg, R.H., Zhang, Z., Battisti, D.S., Golubic, S., 2009.  
 2681 Southward movement of the Pacific intertropical convergence zone AD 1400-1850. *Nature*  
 2682 *Geosci.* 2, 519-525. doi:10.1038/NGEO554

2683 Sachse, D. and Sachs, J.P., 2008. Inverse relationship between D/H fractionation in  
 2684 cyanobacterial lipids and salinity in Christmas Island saline ponds. *Geochim. Cosmochim.*  
 2685 *Acta* 72, 793-806. doi: 10.1016/j.gca.2007.11.022

2686 Sachse, D., Radke, J., Gleixner, G., 2004. Hydrogen isotope ratios of recent lacustrine  
 2687 sedimentary *n*-alkanes record modern climate variability. *Geochim Cosmochim. Acta* 68,  
 2688 4877-4889. doi:10.1016/j.gca.2004.06.004

2689 Sachse, D., Billault, I., Bowen, G.J., Chikaraishi, Y., Dawson, T.E., Feakins, S.J., Freeman,  
 2690 K.H., Magill, C.R., McInerney, F.A., van der Meer, M.T.J., Polissar, P., 10 Robins, R.J.,  
 2691 Sachs, J.P., Schmidt, H.-L., Sessions, A.L., White, J.W.C., West, J.B., Kahmen, A., 2012.  
 2692 Molecular paleohydrology: Interpreting the hydrogen-isotopic composition of lipid biomarkers  
 2693 from photosynthesizing organisms. *Annu. Rev. Earth Planet. Sci.* 40, 221-49.  
 2694 doi:10.1146/annurev-earth-042711-105535

2695 Sáenz, J.P., Wakeham, S.G., Eglinton, T.I., Summons, R.E., 2011. New constraints on the  
 2696 provenance of hopanoids in the marine geologic record: Bacteriohopanepolyols in marine  
 2697 suboxic and anoxic environments. *Org. Geochem.* 42, 1351-1362,  
 2698 doi:10.1016/j.orggeochem.2011.08.016

2699 Sakata, S., Hayes, J.M., Rohmer, M., Hooper, A.B., Seeman, M., 2008. Stable carbon-isotopic  
 2700 compositions of lipids isolated from the ammonia-oxidizing chemoautotroph *Nitrosomonas*  
 2701 *europaea*. *Org. Geochem.* 39, 1725-1734. doi:10.1016/j.orggeochem.2008.08.005

2702 Sarkar, S., Wilkes, H., Prasad, S., Brauer, A., Riedel, N., Stebich, M., Basavaiah, N., Sachse,  
 2703 D., 2014. Spatial heterogeneity in lipid biomarker distributions in the catchment and  
 2704 sediments of a crater lake in central India. *Org. Geochem.* 66, 125-136.  
 2705 doi:10.1016/j.orggeochem.2013.11.009

2706 Sanger, J.E., 1988. Fossil pigments in paleoecology and paleolimnology. *Palaeogeogr.,*  
 2707 *Palaeoclim., Palaeoecol.* 62, 343-359. doi:10.1016/0031-0182(88)90061-2

2708 Sauer, P.E., Miller, G.H., Overpeck, J.T., 2001a. Oxygen isotope ratios of organic matter in  
 2709 Arctic lakes as a paleoclimate proxy: field and laboratory investigations. *J. Paleolim.* 25, 43-  
 2710 64. doi: 10.1023/A:1008133523139

- 2711 Sauer, P.E., Eglinton, T.I., Hayes, J.M., Schimmelmann, A., Sessions, A.L., 2001b.  
 2712 Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for  
 2713 environmental and climatic conditions. *Geochim. Cosmochim. Acta* 65, 213-222.  
 2714 doi:10.1016/S0016-7037(00)00520-2
- 2715 Schaeffer, P., Adam, P., Werung, P., Bernasconi, S., Albrecht, P., 1997. Molecular and  
 2716 isotopic investigation of free and S-bound lipids from an actual meromictic lake (Lake  
 2717 Cadagno, Switzerland). In: *Proceedings of the 18<sup>th</sup> International Meeting on Organic*  
 2718 *Geochemistry*, September 22-26, 1997, Maastricht, The Netherlands, Forschungszentrum  
 2719 Jülich, Jülich, Germany, pp. 57–58.
- 2720 Schefuß, E., Schouten, S., Schneider, R.R., 2005. Climatic controls on central African  
 2721 hydrology during the past 20,000 years. *Nature* 437, 1003-1006. doi:10.1038/nature03945
- 2722 Schefuß, E., Kuhlmann, H., Mollenhauer, G., Prange, M., Pätzold, J., 2011. Forcing of wet  
 2723 phases in southeast Africa over the past 17,000 years. *Nature* 480, 509-512.  
 2724 doi:10.1038/nature10685
- 2725 Schoell, M., Simoneit, B.R.T., Wang, T.G., 1994. Organic geochemistry and coal petrology of  
 2726 Tertiary brown coal in the Zhoujing mine, Baise Basin, South China. Biomarker sources  
 2727 inferred from stable carbon isotope compositions of individual compounds. *Org. Geochem.*  
 2728 21, 713-719. doi:10.1016/0146-6380(94)90014-0
- 2729 Schouten, S., van der Maarel, M.J.E.C., Huber, R., Sinninghe Damsté, J.S., 1997.  
 2730 2,6,10,15,19-Pentamethylcosenes in *Methanobrevibacter smithii*, a marine methanogenic  
 2731 archaeon, and in *Methanosarcina mazei*. *Org. Geochem.* 26, 409-414. doi:10.1016/S0146-  
 2732 6380(97)00011-9
- 2733 Schouten, S., Hoefs, M.J.L., Koopmans, M.P., Bosch, H.-J., Sinninghe Damsté, J.S., 1998a.  
 2734 Structural characterization, occurrence and fate of archaeal ether-bound acyclic and cyclic  
 2735 biphytanes and corresponding diols in sediments. *Org. Geochem.* 29, 1305-1319.  
 2736 doi:10.1016/S0146-6380(98)00131-4
- 2737 Schouten, S., Breteler, W.C.K., Blokker, P., Schogt, N., Rijpstra, W.I.C., Grice, K., Baas, M.,  
 2738 Sinninghe Damsté, J.S., 1998b. Biosynthetic effects on the stable carbon isotopic  
 2739 compositions of algal lipids: Implications for deciphering the carbon isotopic biomarker  
 2740 record. *Geochim. Cosmochim. Acta* 62, 1397-1406. doi:10.1016/S0016-7037(98)00076-3
- 2741 Schouten, S., Rijpstra, W.I.C., Kok, M., Hopmans, E.C., Summons, R.E., Volkman, J.K.,  
 2742 Sinninghe Damsté, J.S., 2001. Molecular organic tracers of biogeochemical processes in a  
 2743 saline meromictic lake (Ace Lake). *Geochim. Cosmochim. Acta* 65, 1629-1640.

2744      doi:10.1016/S0016-7037(00)00627-X

2745      Schouten, S., Ossebaar, J., Schreiber, K., Kienhuis, M.V.M., Langer, G., Benthien, A., Bijma,  
 2746      J., 2006. The effect of temperature, salinity and growth rate on the stable hydrogen isotopic  
 2747      composition of long chain alkenones produced by *Emiliana huxleyi* and *Gephyrocapsa*  
 2748      *oceanica*. Biogeosci. 3, 113–119. doi:10.5194/bg-3-113-2006

2749      Schouten, S., Hopmans, E.C., Sinninghe Damsté, J.S., 2013. The organic geochemistry of  
 2750      glycerol dialkyl glycerol tetraether lipids: A review. Org. Geochem. 54, 19-61.  
 2751      doi:10.1016/j.orggeochem.2012.09.006

2752      Schwab, V.F. and Sachs, J.P., 2011. Hydrogen isotopes in individual alkenones from the  
 2753      Chesapeake Bay estuary. Geochim. Cosmochim. Acta 75, 7552-7565.  
 2754      doi:10.1016/j.gca.2011.09.031

2755      Schwab, V.F. and Sachs, J.P., 2009. The measurement of D/H ratio in alkenones and their  
 2756      isotopic heterogeneity. Org. Geochem. 40, 111-118. doi:10.1016/j.orggeochem.2008.09.013

2757      Segarra, K.E.A., Schubotz, F., Samarkin, V., Yoshinaga, M.Y., Hinrichs, K.-U., Joye, S.B.,  
 2758      2015. High rates of anaerobic methane oxidation in freshwater wetlands reduce potential  
 2759      atmospheric methane emissions. Nature Comm. 6, 7477. doi:10.1038/ncomms8477

2760      Sessions, A.L. and Burgoyne, T.W., Schimmelmann, A., Hayes, J.M., 1999. Fractionation of  
 2761      hydrogen isotopes in lipid biosynthesis. Org. Geochem. 30, 1193-200. doi:10.1016/S0146-  
 2762      6380(99)00094-7

2763      Sessions, A.L., 2016. Factors controlling the deuterium contents of sedimentary  
 2764      hydrocarbons. Org. Geochem. 96, 43-64. doi:10.1016/j.orggeochem.2016.02.012

2765      Showalter, A.M., 1993. Structure and function of plant cell wall proteins. Plant Cell 5, 9-23.  
 2766      doi:10.1105/tpc.5.1.9

2767      Sikes, E., Farrington, J.W., Keigwin, L.D., 1991. Use of the alkenone unsaturation ratio  $U_{37}^k$   
 2768      to determine past sea surface temperatures: core-top SST calibrations and methodology  
 2769      considerations. Earth Planet. Sci. Lett. 104, 36-47. doi:10.1016/0012-821X(91)90235-A

2770      Sinninghe Damsté, J.S., Rampen, S., Irene, W., Rijpstra, C., Abbas, B., Muyzer, G., 2003. A  
 2771      diatomaceous origin for long-chain diols and mid-chain hydroxy methyl alkanoates widely  
 2772      occurring in Quaternary marine sediments: Indicators for high-nutrient conditions. Geochim.  
 2773      Cosmochim. Acta 67, 1339-1348. doi:10.1016/S0016-7037(02)01225-5

2774      Sinninghe Damsté, J.S., Verschuren D., Ossebaar J., Blokker J., van Houten R., van der Meer  
 2775      M.T.J., Plessen B., Schouten S., 2011a. A 25,000-year record of climate-induced changes

2776 in lowland vegetation of eastern equatorial Africa revealed by the stable carbon-isotopic  
 2777 composition of fossil plant leaf waxes. *Earth Planet. Sci. Lett.* 302, 236-246.  
 2778 doi:10.1016/j.epsl.2010.12.025

2779 Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopmans, E.C., Weijers, J.W.H., Foesel, B.U.,  
 2780 Overmann, J., Dedysh, S.N., 2011b. 13,16-Dimethyl octacosanedioic acid (iso-diabolic acid),  
 2781 a common membrane-spanning lipid of *Acidobacteria* subdivisions 1 and 3. *Appl. Environ.*  
 2782 *Microbiol.* 77, 4147-4154. doi:10.1128/AEM.00466-11

2783 Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopmans, E.C., Foesel, B.U., Wust, P.K.,  
 2784 Overmann, J., Tank, M., Bryant, D.A., Dunfield, P.F., Houghton, K., Stott, M.B., 2014. Ether-  
 2785 and ester-bound iso-diabolic acid and other lipids in members of *Acidobacteria* subdivision  
 2786 4. *Appl. Environ. Microbiol.* 80, 5207-5218. doi:10.1128/AEM.01066-14

2787 Smith, B.N. and Epstein, S., 1970. Biogeochemistry of the stable isotopes of hydrogen and  
 2788 carbon in salt marsh biota. *Plant Physiol.* 46, 738-742.

2789 Smittenberg, R.H. and Sachs, J.P., 2007. Purification of dinosterol for hydrogen isotopic  
 2790 analysis using high-performance liquid chromatography–mass spectrometry. *J. Chromatogr.*  
 2791 *A* 1169, 70-76. doi:10.1016/j.chroma.2007.09.018

2792 Spaak, G., Edwards, D.S., Allen, H.J., Grotheer, H., Summons, R.E., Coolen, M.J.L., Grice,  
 2793 K. 2018. Extent and persistence of photic zone euxinia in Middle-Late Devonian seas -  
 2794 Insights from the Canning Basin and implications for petroleum source rock formation. *Mar.*  
 2795 *Petrol. Geol.* 93, 33-56. doi:10.1016/j.marpetgeo.2018.02.033

2796 Stal, L.J., 2015. Nitrogen fixation in cyanobacteria. In: eLS. John Wiley & Sons Ltd.,  
 2797 Chichester. doi:10.1002/9780470015902.a0021159.pub2

2798 Sternberg, L.D.L., 1988. D/H ratios of environmental water recorded by D/H ratios of plant  
 2799 lipids. *Nature* 333, 59-61. doi:10.1038/333059a0

2800 Sternberg, L. and Ellsworth, P.F.V., 2011. Divergent biochemical fractionation, not convergent  
 2801 temperature, explains cellulose oxygen isotope enrichment across latitudes. *PLoS ONE* 6,  
 2802 e28040. doi:10.1371/journal.pone.0028040

2803 Sternberg, L.D.S.L., Pinzon, M-C., Vendramini, P.F., Anderson, W.T., Jahren, A.H., Beuning,  
 2804 K., 2007. Oxygen isotope ratios of cellulose-derived phenylglucosazone: An improved  
 2805 paleoclimate indicator of environmental water and relative humidity. *Geochim. Cosmochim.*  
 2806 *Acta* 71, 2463-2473. doi:10.1016/j.gca.2007.03.004

2807 Stötter, T., Bastviken, D., Bodelier, P.L.E., van Hardenbroek, M., Rinta, P., Schilder, J.,

2808 Schubert, C.J., Heiri, O., 2018. Abundance and  $\delta^{13}\text{C}$  values of fatty acids in lacustrine  
2809 surface sediments: Relationships with in-lake methane concentrations. *Quat. Sci. Rev.* 191,  
2810 337-347. doi:10.1016/j.quascirev.2018.04.029

2811 Strauss, H., 1997. The isotopic composition of sedimentary sulfur through time. *Palaeogeogr.,*  
2812 *Palaeoclim., Palaeoecol.* 132, 97-118. doi:10.1016/S0031-0182(97)00067-9

2813 Street, J.H., Anderson, R.S., Paytan, A., 2012. An organic geochemical record of Sierra  
2814 Nevada climate since the LGM from Swamp Lake, Yosemite. *Quat. Sci. Rev.* 40, 89-106.  
2815 doi:10.1016/j.quascirev.2012.02.017

2816 Summons, R.E. and Powell, T.G., 1987. Identification of aryl isoprenoids in source rocks and  
2817 crude oils: Biological markers for the green sulphur bacteria. *Geochim. Cosmochim. Acta* 51,  
2818 557-566. doi:10.1016/0016-7037(87)90069-X

2819 Summons, R.E., Volkman, J.K., Boreham, C.J., 1987. Dinosterane and other steroidal  
2820 hydrocarbons of dinoflagellate origin in sediments and petroleum. *Geochim. Cosmochim.*  
2821 *Acta* 51, 3075-3082. doi:10.1016/0016-7037(87)90381-4

2822 Summons, R.E., Jahnke, L.L., Roksandic, Z., 1994. Carbon isotopic fractionation in lipids from  
2823 methanotrophic bacteria: Relevance for interpretation of the geochemical record of  
2824 biomarkers. *Geochim. Cosmochim. Acta* 58, 2853-2863. doi:10.1016/0016-7037(94)90119-  
2825 8

2826 Summons, R.E., Hope, J.M., Dowling, L.M., Jahnke, L.L., Largeau, C., Metzger, P., 1996.  
2827 Carbon isotope fractionation in lipid biosynthesis by algae and cyanobacteria. In: Grimalt, J.  
2828 O. and Dorronsoro, C. (eds.), *Organic Geochemistry: Developments and Applications to*  
2829 *Energy, Climate, Environment and Human History*. San Sebastian, Spain: A.I.G.O.A., pp. 6-  
2830 7.

2831 Summons, R.E., Jahnke, L.L., Hope, J.M., Logan, G.A., 1999. 2-Methylhopanoids as  
2832 biomarkers for cyanobacterial oxygenic photosynthesis. *Nature* 400, 554-557.  
2833 doi:10.1038/23005

2834 Summons, R.E., Metzger, P., Largeau, C., Murray, A.P., Hope, J.M., 2002.  
2835 Polymethylsqualanes from *Botryococcus braunii* in lacustrine sediments and crude oils. *Org.*  
2836 *Geochem.* 33, 99-109. doi:10.1016/S0146-6380(01)00147-4

2837 Summons, R.E., Bradley, A.S., Jahnke, L.J., Waldbauer, J.R., 2006. Steroids, triterpenoids  
2838 and molecular oxygen. *Philos. Trans. R. Soc. Lond. B, Biol. Sci.* 361, 951-968.  
2839 doi:10.1098/rstb.2006.1837

2840 Sun, Q., Chu, G.Q., Liu, G.X., Li, S., Wang, X.H., 2007. Calibration of alkenone unsaturation  
 2841 index with growth temperature for a lacustrine species, *Chrysotila lamellosa* (Haptophyceae).  
 2842 Org. Geochem. 38, 1226-1234. doi:10.1016/j.orggeochem.2007.04.007

2843 Swain, E.B., 1985. Measurement and interpretation of sedimentary pigments. Freshw. Biol.  
 2844 15, 53-75. doi:10.1111/j.1365-2427.1985.tb00696.x

2845 Talbot, H.M., Watson, D.F., Pearson, E.J., Farrimond, P., 2003. Diverse biohopanoid  
 2846 compositions of non-marine sediments. Org. Geochem. 34, 1353-1371. doi:10.1016/S0146-  
 2847 6380(03)00159-1

2848 Talbot, H.M., Handley, L., Spencer-Jones, C., Dinga, B.J., Schefuß, E., Mann, P.J., Poulsen,  
 2849 J.R., Spencer, R.G.M., Wabakanghanzi, J.N., 2014. Variability in aerobic methane oxidation  
 2850 over the past 1.2 Myrs recorded in microbial biomarker signatures from Congo fan  
 2851 sediments. Geochim. Cosmochim. Acta 133, 387-401. doi:10.1016/j.gca.2014.02.035

2852 Talbot, M.R., 2001. Nitrogen isotopes in paleolimnology. In: Last, W.M. and Smol, J.P. (eds.),  
 2853 Tracking Environmental Change Using Lake Sediments, vol. 2: Physical and Geochemical  
 2854 Methods, Kluwer, Dordrecht, pp. 401-439.

2855 Tani, Y., Nara, F., Soma, Y., Soma, M., Itoh, N., Matsumoto, G.I., Tanaka, A., Kawai, T., 2009.  
 2856 Phytoplankton assemblage in the Plio-Pleistocene record of Lake Baikal as indicated by  
 2857 sedimentary sterol chlorin esters. Quat. Int. 205, 126-136. doi:10.1016/j.quaint.2009.02.004

2858 Theroux, S., D'Andrea, W.J., Toney, J., Amaral-Zettler, L., Huang, Y., 2010. Phylogenetic  
 2859 diversity and evolutionary relatedness of alkenone-producing haptophyte algae in lakes:  
 2860 Implications for continental paleotemperature reconstructions. Earth Planet. Sci. Lett. 300,  
 2861 311-320. doi:10.1016/j.epsl.2010.10.009

2862 Thiel, V., Jenisch, A., Landmann, G., Reimer, A., Michaelis, W., 1997. Unusual distributions  
 2863 of long-chain alkenones and tetrahymanol from the highly alkaline Lake Van, Turkey.  
 2864 Geochim. Cosmochim. Acta 61, 2053-2064. doi:10.1016/S0016-7037(97)00038-0

2865 Thiel, V., Peckmann, J., Seifert, R., Wehrung, P., Reitner, J., Michaelis, W., 1999. Highly  
 2866 isotopically depleted isoprenoids: Molecular markers for ancient methane venting. Geochim.  
 2867 Cosmochim. Acta 63, 3959-3966. doi:10.1016/S0016-7037(99)00177-5

2868 Tierney, J.E. and Russell, J.M., 2009. Distributions of branched GDGTs in a tropical lake  
 2869 system: Implications for lacustrine application of the MBT/CBT paleoproxy. Org. Geochem.  
 2870 40, 1032-1036. doi:10.1016/j.orggeochem.2009.04.014

2871 Tierney, J.E., Russell, J.M., Huang, Y.S., Sinninghe Damsté, J.S., Hopmans, E.C., Cohen,

2872 A.S., 2008. Northern hemisphere controls on tropical southeast African climate during the  
2873 past 60,000 years. *Science* 322, 252-255. doi:10.1126/science.1160485

2874 Tierney, J.E., Russell, J.M, Huang, Y., 2010. A molecular perspective on Late Quaternary  
2875 climate and vegetation change in the Lake Tanganyika basin, East Africa. *Quat. Sci. Rev.*  
2876 29, 787-800. doi:10.1016/j.quascirev.2009.11.030

2877 Tierney, J.E., Russell, J.M., Sinninghe Damsté, J.S., Huang, Y., Verschuren, D., 2011. Late  
2878 Quaternary behavior of the East African monsoon and the importance of the Congo Air  
2879 Boundary. *Quat. Sci. Rev.* 30, 798-807. doi:10.1016/j.quascirev.2011.01.017

2880 Tipple, B.J. and Pagani, M., 2013. Environmental control on eastern broadleaf forest species'  
2881 leaf wax distributions and D/H ratios. *Geochim. Cosmochim. Acta* 111, 64-77. doi:10.10  
2882 16/j.gca.2012.10 .042

2883 Toney, J.L., Leavitt, P.R., Huang, Y., 2011. Alkenones are common in prairie lakes of interior  
2884 Canada. *Org. Geochem.* 42, 707-712. doi:10.1016/j.orggeochem.2011.06.014

2885 Treibs, A., 1936, Chlorophyll- und Häminderivate in organischen Mineralstoffen: *Angew.*  
2886 *Chemie* 49, 682-686, doi:10.1002/ange.19360493803.

2887 Tulipani, S., Grice, K., Greenwood, P., Schwark, L., Böttcher, M.E., Summons, R.E., Foster,  
2888 C., 2015. Molecular proxies as indicators of freshwater incursion-driven salinity stratification.  
2889 *Chem. Geol.* 409, 61-68. doi:10.1016/j.chemgeo.2015.05.009

2890 Tyler, J., Kashiya, Y., Ohkouchi, N., Ogawa, N., Yokoyama, Y., Chikaraishi, Y., Staff, R.A.,  
2891 Ikehara, M., Bronk Ramsey, C., Bryant, C., Brock, F., Gotanda, K., Haraguchi, T., Yonenobu,  
2892 H., Nakagawa, T., 2010. Tracking aquatic change using chlorin-specific carbon and nitrogen  
2893 isotopes: The last glacial-interglacial transition at Lake Suigetsu, Japan. *Geochim. Geophys.*  
2894 *Geosyst.* 11, Q09010, doi:10.1029/2010GC003186

2895 Uhle, M.E., Macko, S.A., Spero, H.J., Engel, M.H., Lea, D.W., 1997. Sources of carbon and  
2896 nitrogen in modern planktonic foraminifera: the role of algal symbionts as determined by bulk  
2897 compound specific stable isotopic analyses. *Org. Geochem.* 27, 103-113.  
2898 doi:10.1016/S0146-6380(97)00075-2

2899 Urban, N.R., Ernst, K., Bernasconi, S., 1999. Addition of sulfur to organic matter during early  
2900 diagenesis of lake sediments. *Geochim. Cosmochim. Acta* 63, 837-853. doi:10.1016/S0016-  
2901 7037(98)00306-8

2902 van Bree, L.G.J., Rijpstra, W.I.C., Cocquyt, C., Al-Dhabi, N.A., Verschuren, D., Sinninghe  
2903 Damsté, J.S., de Leeuw, J.W., 2014. Origin and palaeoenvironmental significance of C<sub>25</sub> and



- 2904 C<sub>27</sub> *n*-alk-1-enes in a 25,000-year lake-sedimentary record from equatorial East Africa.  
2905 *Geochim. Cosmochim. Acta* 145, 89-102. doi:10.1016/j.gca.2014.08.035
- 2906 van Bree, L.G.J., Peterse, F., van der Meer, M.T.J., Middleburg, J.J., Negash, A.M.D., De  
2907 Crop, W., Cocquyt, C., Wieringa, J.J., Verschuren, D., Sinninghe Damsté, J.S., 2018.  
2908 Seasonal variability in the abundance and stable carbon-isotopic composition of lipid  
2909 biomarkers in suspended particulate matter from a stratified equatorial lake (Lake Chala,  
2910 Kenya/Tanzania): Implications for the sedimentary record. *Quat. Sci. Rev.* 192, 208-224.  
2911 doi:10.1016/j.quascirev.2018.05.023
- 2912 van den Bos, V., Engels, S., Bohncke, S.J.P., Cerli, C., Jansen, B., Kalbitz, K., Peterse, F.,  
2913 Renssen, H., Sachse, D., 2018. Late Holocene changes in vegetation and atmospheric  
2914 circulation at Lake Uddelermeer (The Netherlands) reconstructed using lipid biomarkers and  
2915 compound specific  $\delta$ D analysis. *J. Quatern. Sci.* 33, 100-111. doi:10.1002/jqs.3006
- 2916 van der Meer, M.T.J., Schouten, S., Sinninghe Damsté, J.S., 1998. The effect of the reversed  
2917 tricarboxylic acid cycle on the <sup>13</sup>C contents of bacterial lipids. *Org. Geochem.* 28, 527-533.  
2918 doi:10.1016/S0146-6380(98)00024-2
- 2919 van der Meer, M.T.J., Schouten, S., Rijpstra, W.I.C., Fuchs, G., Sinninghe Damsté, J.S., 2001.  
2920 Stable carbon isotope fractionations of the hyperthermophilic crenarchaeon *Metallosphaera*  
2921 *sedula*. *FEMS Microbiol. Lett.* 196, 67-70. doi:10.1111/j.1574-6968.2001.tb10542.x
- 2922 van der Meer, M.T.J., Baas, M., Rijpstra, W.I.C., Marino, G., Rohling, E.J., Sinninghe Damsté,  
2923 J.S., Schouten, S., 2007. Hydrogen isotopic compositions of long-chain alkenones record  
2924 freshwater flooding of the Eastern Mediterranean at the onset of sapropel deposition. *Earth*  
2925 *Planet. Sci. Lett.* 262, 594-600. doi:10.1016/j.epsl.2007.08.014
- 2926 van Soelen, E.E., Lammers, J.M., Eglinton, T.I., Sinninghe Damsté, J.S., Reichart, G.J., 2014.  
2927 Unusual C<sub>35</sub> to C<sub>38</sub> alkenones in mid-Holocene sediments from a restricted estuary (Charlotte  
2928 Harbor, Florida). *Org. Geochem.* 70, 20-28. doi:10.1016/j.orggeochem.2014.01.021
- 2929 van Winden, J.F., Kip, N., Reichart, G.-J., Jetten, M.S.M., Huub, M.S., Op den Camp, J.M.,  
2930 Sinninghe Damsté, J.S., 2010. Lipids of symbiotic methane-oxidizing bacteria in peat moss  
2931 studied using stable carbon isotopic labeling. *Org. Geochem.* 41, 1040-1044.  
2932 doi:10.1016/j.orggeochem.2010.04.015
- 2933 van Winden, J.F., Talbot, H.M., De Vleeschouwer, F., Reichart, G.-J., Sinninghe Damsté, J.S.,  
2934 2012. Variation in methanotroph-related proxies in peat deposits from Misten Bog, Hautes-  
2935 Fagnes, Belgium. *Org. Geochem.* 53, 73-79. doi:10.1016/j.orggeochem.2012.07.001
- 2936 Vetriani, C., Reysenbach, A.-L., Doré, J., 1998. Recovery and phylogenetic analysis of

2937 archaeal rRNA sequences from continental shelf sediments. FEMS Microbiol. Lett. 161, 83-  
 2938 88. doi:10.1111/j.1574-6968.1998.tb12932.x

2939 Vila, X. and Abella, C.A., 1994. Effects of light quality on the physiology and the ecology of  
 2940 planktonic green sulfur bacteria in lakes. Photosy. Res. 41, 53-65. doi:10.1007/BF02184145

2941 Villinski, J.C., Hayes, J.M., Brassell, S.C., Riggert, V.L., 2008. Sedimentary sterols as  
 2942 biogeochemical indicators in the Southern Ocean. Org. Geochem. 39, 567-588.  
 2943 doi:10.1016/j.orggeochem.2008.01.009

2944 Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter.  
 2945 Org. Geochem. 9, 83-99. doi:10.1016/0146-6380(86)90089-6

2946 Volkman, J.K., Eglinton, G., Corner, E.D.S., Forsberg, T.E.V., 1980a. Long-chain alkenes and  
 2947 alkenones in the marine coccolithophorid *Emiliana huxleyi*. Phytochem. 19, 2619-2622.  
 2948 doi:10.1016/S0031-9422(00)83930-8

2949 Volkman, J.K., Eglinton, G., Corner, E.D.S., Sargent, J.R., 1980b. Novel unsaturated straight-  
 2950 chain C<sub>37</sub>-C<sub>39</sub> methyl and ethyl ketones in marine sediments and a coccolithophore *Emiliana*  
 2951 *huxleyi*. Phys. Chem. Earth 12, 219–227. doi:10.1016/0079-1946(79)90106-X

2952 Volkman, J.K., Barrett, S.M., Dunstan, G.A., 1994. C<sub>25</sub> and C<sub>30</sub> highly branched isoprenoid  
 2953 alkenes in laboratory cultures of two marine diatoms. Org. Geochem. 21, 407-413.  
 2954 doi:10.1016/0146-6380(94)90202-X

2955 Volkman, J.K., Barrett, S.M., Blackburn, S.I., Mansour, M.P., Sikes, E.L., Gelin, F., 1998.  
 2956 Microalgal biomarkers: a review of recent research developments. Org. Geochem. 29, 1163-  
 2957 1179. doi:10.1016/S0146-6380(98)00062-X

2958 Volkman, J.K., 2003. Sterols in microorganisms. Appl. Microbiol. Biotech. 60, 495-506.  
 2959 doi:10.1007/s00253-002-1172-8

2960 Volkman, J.K., 2005. Sterols and other triterpenoids: source specificity and evolution of  
 2961 biosynthetic pathways. Org. Geochem. 36, 139-159. doi:10.1016/j.orggeochem.2004.06.013

2962 Wakeham, S.G., Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2004. Archaeal lipids  
 2963 and anaerobic oxidation of methane in euxinic water columns: a comparative study of the  
 2964 Black Sea and Cariaco Basin. Chem. Geol. 205, 427-442.  
 2965 doi:10.1016/j.chemgeo.2003.12.024

2966 Wakeham, S. G. and Canuel, E. A., 2016. The nature of organic carbon in density-fractionated  
 2967 sediments in the Sacramento-San Joaquin River Delta (California). Biogeosci. 13, 567-582.  
 2968 doi:10.5194/bg-13-567-2016

2969 Weber, Y., De Jonge, C., Rijpstra, W.I.C., Hopmans, E.C., Stadnitskaia, A., Schubert, C.J.,  
 2970 Lehmann, M.F., Sinninghe Damsté, J.S., Niemann, H., 2015. Identification and carbon  
 2971 isotope composition of a novel branched GDGT isomer in lake sediments: Evidence for  
 2972 lacustrine branched GDGT production. *Geochim. Cosmochim. Acta* 154, 118-129.  
 2973 doi:10.1016/j.gca.2015.01.032

2974 Weber, Y., Sinninghe Damsté, J.S., Zopfi, J., De Jonge, C., Gilli, A., Schubert, C.J., Lepori,  
 2975 F., Lehmann, M.F., Niemann, H., 2018. Redox-dependent niche differentiation provides  
 2976 evidence for multiple bacterial sources of glycerol tetraether lipids in lakes. *Proc. Nat. Acad.*  
 2977 *Sci.* 115, 10926-10931. doi:10.1073/pnas.1805186115

2978 Wei, J.H., Yin, X., Welander, P.V., 2016. Sterol synthesis in diverse bacteria. *Front. Microbiol.*  
 2979 7, article no. 990. doi:10.3389/fmicb.2016.00990

2980 Weijers, J.W.H., Schouten, S., Hopmans, E.C., Geenevasen, J.A.J., David, O.R.P., Coleman,  
 2981 J.M., Pancost, R.D., Sinninghe Damsté, J.S., 2006. Membrane lipids of mesophilic anaerobic  
 2982 bacteria thriving in peats have typical archaeal traits. *Env. Microbiol.* 8, 648-657.  
 2983 doi:10.1111/j.1462-2920.2005.00941.x

2984 Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., Sinninghe Damsté, J.S.,  
 2985 2007. Environmental controls on bacterial tetraether membrane lipid distribution in soils.  
 2986 *Geochim. Cosmochim. Acta* 71, 703-713. doi:10.1016/j.gca.2006.10.003

2987 Weijers, J.W.H., Wiesenberg, G.L.B., Bol, R., Hopmans, E.C., Pancost, R.D., 2010. Carbon  
 2988 isotopic composition of branched tetraether membrane lipids in soils suggest a rapid turnover  
 2989 and a heterotrophic life style of their source organism(s). *Biogeosci.* 7, 2959-2973.  
 2990 doi:10.5194/bg-7-2959-2010

2991 Weiss, G.M., Pfannerstill, E.Y., Schouten, S., Sinninghe Damsté, J.S., van der Meer, M.T.J.,  
 2992 2017. Effects of alkalinity and salinity at low and high light intensity on hydrogen isotope  
 2993 fractionation of long-chain alkenones produced by *Emiliana huxleyi*. *Biogeosci.* 14, 5693-  
 2994 5704. doi:10.5194/bg-14-5693-2017

2995 Welander, P.V., Hunter, R.C., Zhang, L., Sessions, A.L., Summons, R.E., Newman, D.K.  
 2996 2009. Hopanoids Play a Role in Membrane Integrity and pH Homeostasis in  
 2997 *Rhodospseudomonas* TIE-1. *J. Bacteriol.* 191, 6145-6156. [https://doi.org/10.1128/JB.00460-](https://doi.org/10.1128/JB.00460-09)  
 2998 09

2999 Werne, J.P., Lyons, T.W., Hollander, D.J., Formolo, M., Sinninghe Damsté, J.S. 2003.  
 3000 Reduced sulfur in euxinic sediments of the Cariaco Basin: Sulfur isotope constraints on  
 3001 organic sulfur formation. *Chem. Geol.* 195, 159-179. doi:10.1016/S0009-2541(02)00393-5

3002 Werne, J.P., Lyons, T.W., Hollander, D.J., Schouten, S., Hopmans, E.C, Sinninghe Damsté,  
 3003 J.S., 2008. Investigating pathways of diagenetic organic matter sulfurization using  
 3004 compound-specific sulfur isotope analysis. *Geochim. Cosmochim. Acta* 72, 3489-3502.  
 3005 doi:10.1016/j.gca.2008.04.033

3006 Whiteside, J.H. and Grice, K. 2016. Biomarker records associated with mass extinction events.  
 3007 *Annu. Rev. Earth Planet. Sci.* 44. doi:10.1146/annurev-earth-060115-012501

3008 Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and  
 3009 oxidation of methane. *Chem. Geol.* 161, 291-314. doi:10.1016/S0009-2541(99)00092-3

3010 Wilson, M.A., Hodgson, D.A., Keely, B.J., 2004. Structural variations in derivatives of the  
 3011 bacteriochlorophylls of Chlorobiaceae: impact of stratigraphic resolution on depth profiles as  
 3012 revealed by methanolysis. *Organic Geochemistry, Advances in Organic Geochemistry 2003.*  
 3013 *Proceedings of the 21st International Meeting on Organic Geochemistry* 35, 1299-1307.

3014 Wirth, S.B. and Sessions, A.L., 2016. Plant-wax D/H ratios in the southern European alps  
 3015 record multiple aspects of climate variability. *Quat. Sci. Rev.* 148, 176-191.  
 3016 10.1016/j.quascirev.2016.07.020

3017 Wissel, H., Mayr, C., Lücke, A., 2008. A new approach for the isolation of cellulose from  
 3018 aquatic plant tissue and freshwater sediments for stable isotope analysis. *Org. Geochem.*  
 3019 39, 1545-1561. doi:10.1016/j.orggeochem.2008.07.014

3020 Withers, N.W., 1987. Dinoflagellate sterols. In: Taylor, F.J.R. (ed.), *The Biology of*  
 3021 *Dinoflagellates*, vol. 21. Blackwell Scientific, Oxford, pp.316-59.

3022 Wolfe, B.B., Edwards, T.W.D., Elgood, R.J., Beuning, K.R.M., 2001. Carbon and oxygen  
 3023 isotope analysis of lake sediment cellulose: methods and applications. In: Last, W.M. and  
 3024 Smol, J.P. (eds.), *Tracking Environmental Change Using Lake Sediments*, vol. 2: Physical  
 3025 and Geochemical Methods, Kluwer, Dordrecht, pp. 373-400.

3026 Wolfe, B.B., Falcone, M.D., Clogg-Wright, K.P., Mongeon, C.L., Yi, Y., Brock, B.E., St. Amour,  
 3027 N.A., Mark, W.A., Edwards, T.W.D., 2007. Progress in isotope paleohydrology using lake  
 3028 sediment cellulose. *J. Paleolimnol.* 37, 221-231. doi:10.1007/s10933-006-9015-8

3029 Wuchter, C., Schouten, S., Boschker, H.T.S., Sinninghe Damsté, J.S., 2003. Bicarbonate  
 3030 uptake by marine Crenarchaeota. *FEMS Microbiol. Lett.* 219, 203–207. doi:10.1016/S0378-  
 3031 1097(03)00060-0

3032 Wuchter, C., Schouten, S., Coolen, M., Sinninghe Damsté, J.S., 2004. Temperature-  
 3033 dependent variation in the distribution of tetraether membrane lipids of marine

3034 Crenarchaeota: Implications for TEX<sub>86</sub> paleothermometry. *Paleoceanogr.* 19, PA4028,  
3035 doi:10.1029/2004PA00104.

3036 Yamaguchi, Y.T., Chikaraishi, Y., Takano, Y., Ogawa, N.O., Imachi, H., Yokoyama, Y.,  
3037 Ohkouchi, N., 2017. Fractionation of nitrogen isotopes during amino acid metabolism in  
3038 heterotrophic and chemolithoautotrophic microbes across Eukarya, Bacteria, and Archaea:  
3039 Effects of nitrogen sources and metabolic pathways. *Org. Geochem.* 111, 101-112.  
3040 doi:10.1016/j.orggeochem.2017.04.004

3041 Yamoah, K.K.A., Chabangborn, A., Chawchai, S., Välranta, M., Wohlfarth, B., Smittenberg,  
3042 R.H., 2016. Large variability in *n*-alkane  $\delta^{13}\text{C}$  values in Lake Pa Kho (Thailand) driven by  
3043 wetland wetness and aquatic productivity. *Org. Geochem.* 97, 53-60.  
3044 doi:10.1016/j.orggeochem.2016.04.008

3045 Yapp, C.J. and Epstein, S., 1982. A reexamination of cellulose carbon-bound hydrogen  $\delta\text{D}$   
3046 measurements and some factors affecting plant-water D/H relationships. *Geochim.*  
3047 *Cosmochim. Acta.* 46, 955-965. doi:10.1016/0016-7037(82)90051-5

3048 York, J.K., Tomasky, G., Valiela, I., Repeta, D.J., 2007. Stable isotopic detection of ammonium  
3049 and nitrate assimilation by phytoplankton in the Waquoit Bay estuarine system. *Limnol.*  
3050 *Oceanogr.*, 52, 144-155. doi:10.4319/lo.2007.52.1.0144

3051 Zech, M., Mayr, C., Tuthorn, M., Leiber-Sauheitl, K., Glaser, B., 2014. Oxygen isotope ratios  
3052 ( $^{18}\text{O}/^{16}\text{O}$ ) of hemicellulose-derived sugar biomarkers in plants, soils and sediments as  
3053 paleoclimate proxy I: Insight from a climate chamber experiment. *Geochim. Cosmochim.*  
3054 *Acta* 126, 614-623. doi:10.1016/j.gca.2013.10.048

3055 Zerkle, A.L., Kamyshny Jr, A., Kump, L.R., Farquhar, J., Oduro, H., Arthur, M.A., 2010. Sulfur  
3056 cycling in a stratified euxinic lake with moderately high sulfate: constraints from quadruple S  
3057 isotopes. *Geochim. Cosmochim. Acta* 74, 4953-4970. doi:10.1016/j.gca.2010.06.015

3058 Zhang, X., Gillespie, A.L., Sessions, A.L., 2009. Large D/H variations in bacterial lipids reflect  
3059 central metabolic pathways. *Proc. Nat. Acad. Sci.* 106, 1-7. doi:10.1073/pnas.0903030106

3060 Zhang, Z. and Sachs, J.P., 2007. Hydrogen isotope fractionation in freshwater algae: I.  
3061 Variations among lipids and species. *Org. Geochem.* 38, 582-608. doi:  
3062 10.1016/j.orggeochem.2006.12.004

3063 Zhang, Z., Sachs, J.P., Marchetti, A., 2009. Hydrogen isotope fractionation in freshwater and  
3064 marine algae: II. Temperature and nitrogen limited growth rate effects. *Org. Geochem.*, 40,  
3065 428-439. doi:10.1016/j.orggeochem.2008.11.002

3066 Zheng, Y., Singarayer, J.S., Cheng, P.C., Yu, Xuefeng, Liu, Z., Valdes, P.J., Pancost, R.D.,  
 3067 2014. Holocene variations in peatland methane cycling associated with the Asian summer  
 3068 monsoon system. *Nature Comm.* 5, 4631. doi:10.1038/ncomms5631.

3069 Zhu, J., Lücke, A., Wissel, H., Mayr, C., Ohlendorf, C., Zolitschka, B., 2014a. Characterizing  
 3070 oxygen isotope variability and host water relation of modern and subfossil aquatic mosses  
 3071 from Laguna Potrok Aike, Southern Patagonia, Argentina. *Geochim. Cosmochim. Acta* 130,  
 3072 212-228. doi:10.1016/j.gca.2014.01.013

3073 Zhu, J., Lücke, A., Wissel, H., Mayr, C., Enters, D., Kim, K.J., Ohlendorf, C., Schäbitz, F.,  
 3074 Zolitschka, B., 2014b. Climate history of the Southern Hemisphere Westerlies belt during the  
 3075 last glacial-interglacial transition revealed from lake water oxygen isotope reconstruction of  
 3076 Laguna Potrok Aike (52°S, Argentina). *Clim. Past* 10, 2153-2169. doi:10.5194/cp-10-2153-  
 3077 2014

3078 Zink, K.-G., Leythaeuser, D., Melkonian, M., Schwark, L., 2001. Temperature dependency of  
 3079 long-chain alkenone distributions in Recent to fossil limnic sediments and in lake waters.  
 3080 *Geochim. Cosmochim. Acta* 65, 253-265.